Materials Issues in Advancing Energy Technologies

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Abstract

Advancing technologies always present questions concerning materials of construction. Sometimes these questions are easily answered: there may even be a choice from existing materials, and there is no limitation on the technology development itself imposed by the limitations of the materials of construction. However, for advancing energy technologies this is seldom the case. This paper will address energy technologies which involve the burning of fossil fuels, such as coal, oil, and natural gas; however, the general principles are similar for heat engines depending on the combustion of biofuels.

Generally, 'advanced' in this context means the attainment of higher temperatures in the overall cycle; and the materials challenges are related to the materials that will be required for the high-temperature components in the system. In situations where the materials of construction present a challenge, it is necessary to examine the processes which lead to materials selection; or materials development; or design compromise.

It is important to recognize that the materials issues are part of the overall engineering design process, and this involves a number of steps:

(1) A market opportunity is identified for a new product (which may be an advance on an old product, or something quite new).
(2) This market opportunity may sometimes be driven by legislation – for example, new environmental limitations.
(3) The desired properties of the new product are identified from analysis of potential customer desires or needs.

Once the characteristics of the new product are defined, a conceptual design is developed. In the first instance, this means designing something that looks as though it will fulfill the identified needs. This conceptual design is 'market tested' – that is, the question "Is this what you wanted?" will be asked, and the people whose job will be to make the product will be brought in, to refine the conceptual design. Once something that looks like an engineering design is developed, a team is created to look at the manufacturing issues.

The economics issues underlie all this – customers are asked at the beginning "You want this – but how much would you pay for it?" and "when do you want it?" as the process proceeds, these questions are always there.

In this paper, the development of this planning approach and its application to the specific issue of high-temperature corrosion will be discussed.

Introduction

This introduction is largely drawn from a recent paper by one of us (JS[1]). It is generally agreed that the first paper on high temperature oxidation was that by G. Tamman (1920)[2], who used interference colors to estimate oxide thickness on steel, 249°C - 392°C, 20 – 56 minutes. This showed a parabolic rate law. In a later paper (1922)[2], he showed that there were different oxidation rates on iron crystals of different orientation, and suggested metal/oxide fit may be a factor. Tamman was aware that the lack of knowledge of the optical properties of iron oxide was a problem, and in 1928 he reported discrepancies between his earlier interference color estimates and results from gravimetric measurements[3]. From the point of view of the present paper, the most important early work was that reported by N. B. Pilling and R. E. Bedworth, who published a paper in 1922[4], which contained the following statements:

- "The corrosion of metals is one problem of great economic interest upon which much time and thought have (*sic*) been expended over a period of many years…….."
- "One somewhat neglected type is the corrosive action of various gases upon metals when exposed to temperatures considerably higher than the atmospheric range……."
- "That the problem is a difficult one to contend with is connoted by the practical dominance of industrial heating by alloys of one type (nickel-chromium). Proprietary interest may account in part for the paucity of information publicly available in the technical literature upon even the most general factors determining the behavior of metals and alloys exposed to such exacting conditions……."
- "Rapidity of corrosion in heated atmospheres is not determined by any property of the metal but by some combination of physical properties of the oxide and its ability to absorb and diffuse oxygen"

Pilling and Bedworth worked in the Research Laboratory of the Westinghouse Electric and Manufacturing Company, and it is apparent from their remarks that in fact the use of heater alloys and the study of their high-temperature corrosion resistance in service had already been in progress for some time at the date of their presentation.

The following year they presented their rather better known paper to the Institute of Metals in England[5], and this was followed by some interesting discussions, one by Ulick R. Evans. Evans published his textbook on "The Corrosion of Metals" in 1924[6], and pages 12 – 22 in that discuss high-temperature oxidation, largely based on the Pilling and Bedworth paper. Pilling and Bedworth also reported generally parabolic oxidation rates, at higher temperatures and longer times than those of Tamman, and suggested that the temperature dependence of the rate constant followed a power law. In 1926, J. S. Dunn[7] commented that a power law had no physical significance, and replaced it with the Arrhenius equation; actually both fitted the data equally well! He also criticized Tamman's interference technique on optical grounds. In 1931 he oxidized Cu – Zn alloys, and showed great improvement in the oxidation of Cu – 30%Zn by the addition of relatively small amounts of Al; these data were quoted by Wagner in what is usually called his 'secondary getter' paper[8].

In 1929, L. B. Pfeil published[9] an extensive paper on the basis of his study of the oxidation of steel at temperatures in the range 750 – 1050°C, for times up to 10 days; in this work (which was conducted at the University of Swansea) he also studied the Fe – O phase diagram. He remarked on the presence of three distinct oxide layers; that in contact with the metal was identified as 'ferrous oxide' with a composition close to FeO; the middle layer was magnetite, and the outermost layer was hematite. He also reported that the "inner surface of layer 2

corresponds exactly in position and surface characteristics with the original surface of the unoxidized iron".

All of these studies understood clearly that the observed kinetics were consistent with the diffusional transport of one or both reactants through the continuous oxide layer. Pilling and Bedworth considered mostly the case where oxygen was transported inward; Pfeil argued for the transport of metal outwards, largely on morphological grounds. Pfeil also considered what he termed a 'countercurrent' transport process. Dunn's introduction of the Arrhenius relationship for the temperature dependence of the rate constant was based on his belief that the transport process was indeed a thermally-activated classical solid-state diffusional transport.

However, there was essentially no understanding of the details of the transport mechanism. The development of the first detailed theories of the transport processes traces back to 1926, when J. Frenkel[10] introduced the idea of a defect in the lattices of crystalline compounds. This in turn eventually led to Carl Wagner's important model for the transport processes associated with chemical reactions, in 1933[11].

The point of this very brief history is because these early papers to a significant extent describe nearly all the features of our current perceptions of our subject. In between 1920 and 1932, there were approximately 64 papers published on high-temperature oxidation. Over the next ten years, a further 155 papers were published. The first major book devoted entirely to this subject was Oxidation of Metals and Alloys, by O. Kubaschewski and B. E. Hopkins[12], both of whom were at the time at the National Physical Laboratory in England. The first edition of this was published in 1953, and contained 549 references. While not all of these papers were directly on high-temperature oxidation (there was a significant section on diffusion, for example) it is clear that there had been a substantial expansion of activity in the field. We suggest that this is a perfect model for a textbook, not least because of its very comprehensive list of references to the original research papers. The second edition was published in 1967, and by this time the reference list had grown to 950.

In the autumn of 1969, the first issue of the journal Oxidation of Metals was published, under the editorship of D. L. Douglass. Over the course of the 31 years up to the completion of volume 54, approximately 1200 papers have been published. By no means all of the papers on high-temperature oxidation and corrosion have appeared in Professor Douglass's pages, but this gives at least a general feeling for the enormous research output on this topic within the last three or four decades.

The changes within this time have been significant in some ways, particularly in the experimental techniques used to study the reactions and the evolution of our thinking about the processes involved. The underlying driver, however, is the same as it was in 1920: the need for metals and alloys that can provide adequate mechanical properties and adequate service lifetimes in environments which combine high temperatures and aggressive chemistry. For a number of areas of technology, the ability to provide such materials essentially paces the development.

As the importance of the underlying driver became recognized, and increasingly support for research in this field came from funding programs with this as a major concern, the pattern of the research being conducted, both in industrial research laboratories and in academic institutions, changed in character. One major change was the recognition that if you wanted high-temperature oxidation resistance, you were going to have to study the formation of alumina (Al_2O_3), chromia (Cr_2O_3), and (just possibly) SiO_2 scales, as well as the ability of a wide range of alloys, optimized for other properties, to retain them during thermal cycling, elastic deformation, and chemical shifts for prolonged periods of time. Another important area was the 'oxidation' of materials in much more complex environments.

Progress in the Field Over the Last Forty Years

The changes that have taken place over the last forty years could be summarized as follows:

Greater attention to the characterization of the oxidizing system
In the first edition of Kubaschewski and Hopkins' book there were, to all intents, no discussions of the morphology of the oxidizing systems, and essentially no micrographs (although of course such observations were being made, particularly by investigators in industry). At the beginning of the last forty years this changed; really quite abruptly.

The techniques available for characterization have progressed enormously: conventional optical metallography improved greatly over the first few years, although it then went into an (ill advised) decline; there is some reason to believe that the information that can be better derived from this method than from some of the newer techniques is once again being recognized. However, the introduction of Electron Probe Microanalysis (EPMA) and also Scanning Electron Microscopy (SEM) led to many important advances in understanding the development of high-temperature oxide scales. The possibility of conducting oxidation experiments *in situ* by means of molecular beams and differential pumping has been a more recent development. Transmission electron microscopy (TEM) has presented more difficulties, because of the problems (a) in preparing a thin foil of the metal/oxide interface; and (b) assuring oneself that any suitably electron-transparent section produced was representative. Latterly, the development of ion beam thinning techniques has reduced the sample preparation problems very greatly.

Overall, in the course of the last fifteen years the ability to characterize the oxidizing system both structurally and chemically at a very fine scale has improved enormously, using a wide range of sophisticated techniques.

Part of the motivation for the growth in the application of characterization techniques has been driven by basic research; but the reason for the early application of these techniques was because it was recognized that an important consequence of oxidation is the degradation of the mechanical properties of the component, and this is only partly related to the removal of material to form the oxide scale: intrusion of oxide products into the substrate, and depletion of alloying elements are even more important in some situations.

Decrease in the interest in reaction kinetics as a fundamental issue
The matter of whether or not the reaction rate can be described as a parabola, or any other functional form, has been of progressively less interest to investigators. Of course, in terms of life prediction of a component, or as a means of identifying the nature of the important transport processes, there is still some reason to go through the routine of kinetic analysis, and measurement of the activation energy; but other factors have been recognized as much more important in life prediction.

Recognition of the importance of 'short-circuit' transport of reactants
Following Wagner, there was for many years an underlying feeling that the important transport processes for the reactants were through the bulk crystalline oxide. While early investigators (U. R. Evans, for example) understood that transport through other paths, such as cracks or grain boundaries, was a possibility, it is only relatively recently that investigators have come to understand that bulk diffusion through the oxide lattice as a transport process for the reactants is the exception rather than the norm; and that this is particularly true for the oxides formed on high-temperature alloys in service environments.

Greatly increased awareness of the importance of scale failure
The whole issue of scale failure, and hence the related issues of stress generation and relaxation, scale/substrate adhesion, the effect of thermal cycling as part of the duty cycle in service, and the in-service elastic deformation of the substrate, have been recognized as being very important. Of course, some of these issues were mentioned by Pilling and Bedworth right at the beginning, but the fact that the only aspect that was mentioned for much of the time up to the 1960's was the 'Pilling-Bedworth Ratio' shows how little understanding there was. Of course, as always, there were pioneers throughout the whole period who discussed these issues, but they made little impact on the mainstream.

The growth of surface modification as an approach to the problem
The idea of using surface modifications, including aluminizing and other diffusion processes, and coatings as a means of separating the mechanical requirements and the oxidation resistance requirements of a component, is again of considerable antiquity. However, often pressure from design engineers (who hated coatings!) meant that this was always regarded as a last resort. All that changed, as a result of a number of advances: higher-temperature industrial chemistry, notably in the petrochemical industry; and of course the rise in importance of the aviation gas turbine. Coatings as a systematic approach to the problem have become a major component of our field.

The recognition of the rôle of minor constituents in the alloys, the coatings, and the environment on the oxidation degradation processes
Once again, many of these aspects were qualitatively known, usually as specific industry problems, early on; and of course the key discoveries of what is now call the Reactive Element Effect were made by Pfeil in England and Hessenbruch in Germany around 1940 – 42. The effects of minor elements on the adhesion of iron oxides to steels during hot rolling were discussed early on: the objective here was to *decrease* the scale adhesion! However, over the last forty years this aspect has received much more attention, and the deleterious effect of sulfur in superalloys and coatings on the adhesion of protective alumina scales has resulted in a great deal of careful research of this aspect over the last several years. Interestingly, the effect was reported virtually simultaneously by three widely-separated investigators!

A growing awareness of the importance of breakaway, and the need for long-term testing
In the majority of situations, the high-temperature components are required to have very long *assured* lifetimes – of the order of several thousand hours. The sort of short-term exposures that can be conducted within university research programs are of limited value, because often the reaction will undergo a significant change, and frequently an acceleration, at times which are considerably greater than 100 hours, but still very short in relation to the required lifetime. Once again, this sort of behavior was described early on, but little significant research was directed towards understanding and predicting it. Over the last few years, much more attention has been addressed to this issue, although it is fair to say that as yet our understanding is still very incomplete.

An improved understanding of the dangers of 'accelerated testing'
This is closely related to the previous item. In order to grow scales thick enough to resemble scales grown in service, but without committing many thousands of hours to tests, the temptation is to accelerate the reaction. Such acceleration may be done by increasing the temperature, or by increasing the severity of the environment chemistry. The danger of excessive temperature was recognized in the very early days, because much of the interest then was in the oxidation of plain carbon steel: it is well-known that service temperatures are less than $500^{o}C$, for strength reasons: however, below $570^{o}C$, only hematite and magnetite are stable oxide phases. If one raises the test temperature to (say) $650^{o}C$, wustite (FeO) becomes stable, and this grows much more rapidly than the other two oxides. There is a related problem with alumina scales at much higher temperatures: the major transport processes at

temperatures of the order of 1000°C are short-circuits; but since the activation energies for these are much lower than those for the intrinsic lattice diffusion processes, the contribution of the latter will become dominant if the temperature is high enough. There have been similar problems with increasing the aggressiveness of the chemical environment, for example with systems for which the major issue is molten salt accelerated attack.

Issues of this kind have resulted in a much greater interest in testing procedures altogether, with the aim of developing tests that are (a) objective, in the sense that different investigators using them will produce comparable results; (b) relevant, in that they rank materials in the same order as the practical experience, where relevant data exist; and (c) quantitative, in that they ultimately will be capable of generating data that can be used with confidence by design engineers.

Probably, most of those in the field would agree that the list above produces a picture of our field that is significantly different to the picture we would have produced forty years ago.

So What About the Next 40 Years?

"Prediction is very difficult; particularly of the future". This quotation, or some form of it, is attributed to at least three different sources! However, for the nearer term prediction is usually done by an 'informed extrapolation of the immediate past'.

The increase in the concentration on research directed toward critical applications that has been one of the major, and continuing, evolutions of the last forty years must continue; and this does not simply mean that the oxidation researcher reacts to demands from design engineers. The next generation of researchers must become even more aware of the integrated system approach to advanced development, and thus recognize that they need to be able to participate in the engineering aspects. For some time oxidation researchers have understood that issues related to materials production and fabrication are part of their responsibility.

A major driver for higher-temperature capable materials is the need to achieve higher efficiencies in heat engines. The primary reason for this is to reduce fuel costs, of course; but there is also a number of environmental issues which are also important. One example is the desire to reduce emissions of CO_2 and other gases that may lead to global warming. The efficiency of a heat engine, which converts thermal energy to mechanical energy, has a theoretical maximum value which was demonstrated by Carnot: the Carnot efficiency is:

$$\eta_c \quad = \quad (T_{max} - T_{min})/T_{max}$$

where T_{max} is the maximum temperature in the thermodynamic cycle, and T_{min} is the minimum temperature, both as absolute temperatures. The actual efficiency is always less than the Carnot efficiency, in part because of irreversibilities in the practical, as opposed to the ideal cycle; and in part because of losses of one sort and another. Nevertheless, the path to improved efficiency is related to increasing the maximum temperature, and reducing the minimum temperature. In practical terms, the minimum attainable temperature will be the ambient temperature, so generally the march to higher efficiencies involves increasing the maximum temperature. Practical heat engine cycles are (1) the Rankine cycle, which involves the boiling of water to form high-pressure steam which is then expanded through a turbine to produce mechanical work, and condensed at the back end; (2) the Brayton cycle in which a gas (for example, air) is compressed, heated, typically by injecting fuel which is burnt, and then expanded through a turbine; (3) the Otto cycle and (4) the Diesel cycle, which are those utilized in internal combustion engines; and (5) the Stirling cycle, which is a closed

cycle with the heating and cooling of the working fluid accomplished through heat exchangers.

For operational reasons, the bulk of the electricity generated world wide at the moment is by Rankine cycle boiler/steam turbine systems, with the turbine shaft driving a generator. The maximum steam temperature increased progressively until perhaps fifty years ago, when it reached the current level of approximately $542^{o}C$ (in the US). The overall efficiency of the system is approximately 0.36; environmental control systems that are required to reduce harmful emissions in the exhaust gases carry an efficiency penalty. However, there is currently a number of programs in different parts of the world aimed at increasing the main steam temperature to $650^{o}C$, or even higher. It is claimed that this offers the possibility of increasing the overall efficiency to 0.48.

It is possible to use the exhaust heat from a gas turbine to power a 'bottoming' Rankine cycle; this is then called a 'combined cycle'. The exhaust temperature from a gas turbine is relatively high, and the efficiency is not as high as one might suppose, given the high maximum temperature. Overall, this takes the benefit of the high maximum temperature in the Brayton cycle with the low minimum temperature in the Rankine cycle: efficiencies close to 0.60 have been achieved with advanced systems of this type.

As an example, perhaps the most critical part of this materials area at the moment is the aim to increase the maximum working temperature in a gas turbine. As the development of this Brayton cycle machine has progressed, particularly as a result of its use as motive power plants in aircraft, the progression has involved:

- The development of nickel-, cobalt-, and to a lesser extent, iron-base alloys with improved high-temperature mechanical properties;
- The cooling of the hot components, by forming internal channels through which relatively cold air is pumped;
- The application of low thermal conductivity layers on the hot surface, coupled with the internal cooling, to enable a higher working fluid temperature to be attained while keeping the temperature of the metallic component at permissible levels. These are called 'thermal barrier coatings' (TBCs).

The TBC-protected high-temperature inlet stages of an advanced gas turbine are about as completely integrated an issue as one can imagine: the dynamic oxidation process is that of the bond coating layer between the single crystal superalloy component and the yttria-stabilized zirconia thermal barrier coating. There are mobile chemical components of the alloy itself and the bond coating alloy (which is generally an MCrAlY or a platinum aluminide), and possibly also from the ceramic thermal barrier coating, as well as the oxidizing species which include oxygen, nitrogen, water vapor, and combustion products from the fuel. There is a possibility of alkali salt components carried in with the intake air or shed from the compressor. The thermal situation involves not only the thermal cycling associated with stopping, starting, and load changing parts of the duty cycle, but also the thermal flux from the external environment through to the coolant within the cooling passages of the component. In service, the metallic components undergo elastic flexing to varying degrees, with the rotors and turbine blades experiencing, in addition, large centrifugal loads. Another aspect is related to the structure of the coatings, both the bond coating and the thermal barrier: there are several methods by which these can be fabricated, and there are systematic differences in the morphologies as a result. On top of that, there are issues related to the consequences of a local failure in service.

It is necessary for anyone interested in conducting research on the role of oxidation in this system to have a good understanding of all these aspects. But beyond this, it may turn out that greatly improved lifetimes might be attainable if some aspects of the operational envelope could be modified; and in that case the investigator should have at least a general idea as to what is possible and what is not. For example, in an application where the gas turbine is land-based as part of an integrated combined cycle generator, it might be possible to modify the start-up procedures to reduce the thermal shock; if the engine is to be used in a commercial aircraft, the ability to do that is much more limited; if the engine is to be used in a military fighter aircraft that option would simply not be available. This is a greatly oversimplified description of a system problem that is much more complex!

How to Plan a Research Program for Materials for the Future

A Roadmap is a blueprint for the attainment of an industry's vision for the future positioning of its business, or for a governmental agency to achieve a desired improvement in, for instance, national health, energy, or other infrastructure. In the case of an industry, the Roadmap is typically focused on the development of products or capabilities sufficiently advanced over the present that their successful development would result in a market leadership position.

The Roadmap planning method is rather different from the more usual strategic planning approach, although both are concerned with longer range, macroscopic issues. The key characteristics of the Roadmapping approach can be summarized as follows.

- In the Roadmapping approach the first step is to define a number of desired targets, which are called Destinations.
- The number of Destinations in any given Roadmap is small: five is generally regarded as a maximum.
- A Destination marks an important target that must be attained if the future Vision is to be reached. It is quantitative – that is, not simply "Efficiencies will be improved" but "An efficiency of 0.65 will be attained" – and also quantitative in terms of delivery date – "This efficiency will be attained by the end of 2006".
- The Destinations are defined as a result of consensus among those individuals or groups of individuals with a specific involvement with the future of the entity (business) concerned. These individuals are called the Stakeholders.
- Stakeholders are not limited to those within the entity itself. For example: customers (actual and potential); impacted groups (this could include environmental issues, for example); suppliers; other components of the larger group within which the entity is embedded (in the case of a business, the entity may be a division within the business, and this refers to other divisions within the same business).
- The Roadmap is a dynamic entity, and it must be reviewed continually. Changes in the Roadmap may be required because of changes in the outside world, or because experience developed within the research and development program that is a result of the Roadmapping process shows that specific Destinations cannot be attained as defined.

The concept of the Stakeholder Group is crucial to the Roadmapping method. It will, in essence, 'own' the Roadmap; and is responsible for committing to provide the necessary support, whatever that may be. In the past, an entity would develop a Strategic Plan, and then that Plan would have to be 'sold' to those whose support would be necessary; the ownership for the Plan always remained with the entity. In the Roadmap approach, the selling in effect is done as part of the planning process itself.

In the case of major business areas one can imagine a number of different Roadmaps; and in some cases it is easy to see that there may be a hierarchy of Roadmaps. For some businesses, materials considerations are paramount, e.g. semiconductors: the development of new materials technology is inextricably linked to the ability to develop and process improved or new semiconductors or device architectures. In this case, the overall *Product Roadmap* explicitly embodies a *Materials Roadmap*. The International Technology Roadmap for Semiconductors (ITRS) is an assessment of the semiconductor technology requirements and identifies the technological challenges and needs facing the semiconductor industry over the next 15 years. The objective of the ITRS is to ensure advancements in the performance of integrated circuits. This assessment is a cooperative effort of the global industry manufacturers and suppliers, government organizations, consortia, and universities. International SEMATECH is the global communication center for this activity: details of the Roadmap can be found at http://public.itrs.net.

In other businesses, the ability to reach the destinations may be highly dependent on the use of improved materials, but the availability (or lack) of such materials may not be addressed until the more detailed, later stages of the roadmapping process. By the time this point is reached, the cost or timing associated with obtaining the required materials may be significantly at odds with those of the overall Vision, such that radical revision of the Destinations may be necessary. As a consequence, in cases such as these, the association of a Materials Roadmap with each Product Roadmap is a prudent step to providing a means for rapidly examining the materials options for attaining the performance goals set by the demands of a given Product Roadmap

Materials Roadmaps
The functions of Materials Roadmaps associated with any Product Roadmap are similar, even though the types of materials and properties needed to enable any given Product Roadmap may be quite different.

Specifically, a Materials Roadmap should:

- provide the capability to assess the properties of existing materials
- provide information on availability and cost of production and fabrication
- provide the means for examining alternative strategies when the set of properties desired cannot be found in current materials

The steps required to establish a Materials Roadmap will be something like this.

1. From the Product Roadmap, define the components involved and specific materials issues associated with each destination: that is, compile a 'Materials Needs' statement.
3. Differentiate between issues requiring data-mining efforts, manufacturing-type efforts, and R&D.
4. Flag the existence of materials barriers (perceived or absolute) to achieving required capabilities.
5. List Destinations that involve technologies where the materials capabilities required are beyond those currently available. This requires a detailed understanding of the Destinations and the associated expectations for materials.
7. Indicate specific problems/limitations, and current work in progress to address these issues.
8. Provide an estimation of the time frame for success, and costs for practical realization.

The managers and stakeholders of the Materials Roadmap must interact with the Product Roadmap stakeholders on a regular basis to determine if changes in, for instance, the market need, have affected specific destinations which will impact on materials consideration. In addition, it is necessary to feed back to the Product Roadmap stakeholders any materials limitations that could impact timing or ability to attain current or revised destinations.

The specific materials properties required and the time frame for their application are derived from the Product Roadmap, and include not only the physical/mechanical properties, operating temperature range, and required service lifetime of the components, but also the availability of procedures for manufacture and assembly into the final product, and any cost and time constraints. To be able to rapidly assess the available options, the developers of the Materials Roadmap must possess detailed information of the applicable classes of materials, as well as sufficient knowledge to allow the rapid identification of potential materials barriers. The Materials Roadmap 'Toolbox,' therefore, must include databases of the capabilities and limitations of available materials; be capable of assessing the probable applicability of new classes of materials; and have the resources to evaluate the feasibility of incremental improvements or the need for new approaches. There is also an implicit need for an awareness of the status of R&D programs (worldwide) that are addressing (or have addressed) the removal of any perceived materials barriers.

For current materials, much of the information required is usually available, although some may be limited by commercial confidentiality. Appropriate identification of stakeholders for the Materials Roadmap should address this issue.

For Materials Roadmaps aimed at longer-range and ambitious visions, it is important to have an idea of what can be done; what might be possible with further developments of the kind that have been in progress for some time; what is going to require significant breakthroughs; and what is impossible. The initial activity may conclude that the needed materials capabilities do not exist, which obviously will have major consequences for the Product Road Map.

Problems for High-Temperature Materials for the Next Thirty Years

The Materials Roadmap described above is defined by a Product Roadmap aimed at a specific product. However, the further one looks into the future, the more difficult it becomes to identify specific products: the Destinations for the longer-term Roadmaps are more broadly defined, and often they have aspects which are societal and political in character. For example, EPRI's *Electricity Technology Roadmap – Powering Progress* includes some Destinations which relate to the fairly near future – for example, strengthening the power delivery infrastructure – which permit the definition of needed products, and thus Product Roadmaps, and hence associated Materials Roadmaps, can be defined. However, other Destinations relate to providing electricity to the entire future population of the world at a level sufficient to ensure a minimum level of well-being for everyone. It is hard to define what the products are that will enable the attainment of this Destination, and consequently no Materials Roadmaps could be designed that would be useful.

Thirty years is probably a point in the future where incremental evolutionary developments in existing technologies will not be sufficient. In this case, we have to think of a different kind of Materials Roadmap, which is concerned with the discovery and development of new classes of materials that will have properties that will transcend what is now possible – perhaps beyond what can be currently regarded as conceivable!

One of the most pressing materials needs for the not to distant future appears to be for approaches that will allow materials that are capable of broad industrial application to be used at higher temperatures than are currently attainable. Two major routes seem possible: first, to

cap all previous incremental improvements by maximizing the strength capabilities of current alloys by the application of the latest understanding of composition-structure-property interactions, without straying too far from the original alloy compositional specifications so that the same processing routes can be used.

The second approach would be a leap forward, and would involve the development of strengthening mechanisms with even higher-temperature capabilities, and their combination with materials processing innovations, that would make them available for use at affordable prices.

For the field of High-Temperature Oxidation and Corrosion, it is probable that such developments will involve some level of novelty, since balancing the requirements for thermodynamic stability of strengthening phases with those for protective scale formation seemingly become increasingly incompatible with increasing temperature. Such research is almost guaranteed to be relatively slow, in part because there is a number of steps in moving to a material based on new concepts. Such ideas must be followed by laboratory-based research, and this then has to be moved into a possible product material or materials that can be tested in the appropriate range of conditions. Once a new conceptual material is produced, a possible application or applications have to be identified, and the new possibilities that the new material enables have to be defined. This will then require a new and more specific range of tests to be performed. If all goes well, the ability of the new materials concept to be incorporated into a system, and the development of a manufacturing and fabrication route will be required.

It is important to differentiate this advanced type of Roadmap from the Edisonian-based technical-push rather than market-pull approach sometimes viewed as the role of 'basic science.' In this case, while specific targets cannot be set for the properties to be attained, the barriers to be removed are readily defined, and clear steps with associated tests ('milestones') can and should be used to evaluate the potential of any approach.

Given all this, for something to appear in an application thirty years from now, it is probable that the underlying concept either currently exists, or it will appear within the next 5 to 10 (at the outside!) years.

In the class of material concepts that already exist, but need further research for them to help in important advances, one might list

- Oxide dispersion-strengthened (ODS) alloys.
- High-temperature intermetallics, such as Laves phases and Engel-Brewer phases.
- Non-oxide ceramics, such as carbides and nitrides.
- Engineering oxide ceramics.

In the case of ODS alloys, the problems are well-known: highly anisotropic properties as presently made; problems in ensuring reproducible product properties; and problems in joining, either to itself or to other system components. However, all of these issues are currently under investigation; but they have been under investigation for several years and the approach to an acceptable material has been disappointingly slow.

High-temperature intermetallics have received less study, except for the aluminides. There are niche markets where they are acceptable now; but, once again, the research on the aluminides has been in process for a significant number of years, and the advances to the point of being what can be called a 'disruptive technology' in Clayton M. Christensen's term (*The Innovator's Dilemma*, 1997) have still not taken place. The challenge for the other

11

intermetallics is considerably greater. Perhaps the greatest opportunity is in the refractory silicides.

Non-oxide ceramics for structural application have recently received more attention, particularly silicon nitride, and silicon carbide composites. Silicon nitride is favored because of its toughness and strength, whereas silicon carbide is used in composites as a way of developing toughness, and has found application in combustion environments. It is interesting that SiAlON, which was regarded as the likely winner twenty years or so ago, appears to have disappeared from consideration for structural applications, although it is used in non-structural applications, and may have a role in ceramic composites.

Engineering oxide ceramics have gained a secure position in a number of niche applications, of course. However, while there have been repeated efforts to develop oxide ceramics whose toughness is adequate for gas turbine hot section components, it appears that non-oxide ceramic composites will be more successful in these applications. There has also been a number of developments for components in high-temperature fuel cells.

Obviously, there will be environmental issues for all of these classes of materials, but it is not always easy to predict what the issues may be. Recently, there has been an increase in interest in the effect of water vapor on high-temperature corrosion, and some of the advanced materials have shown sensitivity to this. There is as yet very little known about the effect of contaminants, either in the environment or in the alloys themselves.

Research opportunities recognized but, as yet, not fully developed include, for example, the mechanisms for inducing breakaway acceleration in corrosion in service; this is an important factor in remaining life prediction.

Over the last several decades we have discovered a number of important effects attributable to minor constituents in the alloys, positive in the case of the 'reactive elements'; negative in the case of sulfur. In spite of a great deal of research, there is still not sufficient understanding of the underlying mechanisms to allow the prediction of the effects of minor additions that have not yet been examined. Nowadays, a major thrust in all applied science has been to develop fundamentally-based models, capable of being able to make predictions. This is, to say the least, highly desirable when one is concerned in making predictions of the service lifetime of materials that have not been made in systems that have yet to be defined!

Another area that has developed in recent years has been the recognition that the answers to our materials problems will be with 'materials systems', rather than single component materials. This awareness can be traced to the understanding that, in order to accommodate the increased firing temperatures needed for higher power, the first stages in a gas turbine had to involve components involving complex internal cooling passages and external coatings. This recognition dates from around 1970 or so; but it became recognized for what it was - a materials systems solution – with the addition of the thermal barrier coating a few years ago. It is important to build this conceptual basis into all of our research in the future.

Finally, and to repeat a statement made several times above, it is important to remember that the 'materials system' is intrinsically embedded into an 'engineering system', and the constraints and opportunities that this presents are not simply matters that the corrosion specialist receives from others. The concept of systems integration must extend to the researcher as well as to the research!

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