Fossil-fuelled power generation





Materials UK Energy Review 2007 Report 2 - Fossil-fuelled Power Generation

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Fossil-fuelled power plants currently provide over 70% of the UK's electricity generating capacity and will remain a major source of energy for the foreseeable future.

The ageing fleet will be replaced and plans are already in place to build modern high efficiency power stations, together with a large-scale carbon capture and storage demonstration plant, bringing with it new materials challenges.

The UK remains a centre for technical excellence in fossil energy materials, particularly high temperature materials and coatings. A high proportion of the original equipment manufacturers (OEMs) have key activities located within the UK and most have retained Materials Technology and R&D as key activities. The UK needs to enhance this expertise to remain at the forefront of future materials technology in fossil energy.

The key drivers for fossil-fuelled power generation are to minimise:

- 1 The impact on the environment through reduction of CO_2 emissions.
- 2 Cost (original manufacturer, ownership/use and end of life disposal).

Current estimates are that coal and gas plant efficiency can be improved by up to 20% over current levels. For a 500MWh coal station this equates to a reduction in CO_2 emissions from 0.9Mt/year to 0.74Mt/year, while for an equivalent gas fired station the reduction would be from 0.36Mt/year to 0.29Mt/year.

Executive summary

There is the opportunity for the UK to become world leaders in Carbon Capture and Storage (CCS) technologies and to reduce CO₂ emissions from fossil fuel power generation by up to 90% by deployment of CCS. However adoption of such technologies can lead to reduced plant efficiencies of >10%, therefore the adoption of a twin track approach of improved efficiency and use of carbon capture technologies is essential. Co-firing with renewable fuels will also be used to reduce emissions. All of these technologies involve components operating in severe, aggressive environments with significant implications on the materials being used. The three key areas for materials technology development are therefore related to;

- 1 Increasing plant efficiency
- 2 Co-firing with renewable fuels
- 3 CO₂ sequestration

This report reviews the current available technology for each of the key types of fossil energy generating plant and associated technologies. It identifies specific short and medium term R&D required to meet the challenges. Key long-term developments are also outlined. The identified research programmes are integrated into a framework with common research themes.

Key recommendations

- 1 The UK should develop an integrated structure for Energy Materials development combining the work being funded by industry, the research councils and other bodies. This will enable developments to be funded at an appropriate level, carried out in a holistic manner and delivered at appropriate timescales. The infrastructure needs to span from the laboratory (academic) scale through to full-scale (industrial) validation and must include the inputs from other stakeholders, such as The Energy Technologies Institute.
- 2 The high level Materials R&D framework over 5, 10 and 20 years timescales is;

5 years

- Incremental changes in current materials sysyems
- Production and characterisation of prototype components manufactured using identified materials and processes.
- Repair and improvement solutions for existing plant and materials.
- Advanced manufacturing development for existing materials systems and processes aimed at cost reduction and increased performance and integrity.

10 years

- Development of new material systems (substrate and coatings) based on existing knowledge including behaviour in realistic and increasingly aggressive environments
- Development and application of process modelling to new materials to speed up introduction and help define new system solutions.
- Adopting a total system approach to critical part design and life prediction with multi-material components with joints and coatings.

20 years

- Identification of disruptive novel material systems and initial characterisation to identify most promising approaches
- Development of novel advanced technologies that will enable high overall efficiencies, significantly reduce emissions and provide high reliability
- 3 In addition there is an ongoing requirement for fundamental research in the following underpinning, generic areas without which recommendation 2 cannot be delivered:
- Surface protection technologies (Coatings).
- Improved understanding and predictive modelling of degradation mechanisms (Lifing).
- Non-invasive inspection techniques for in situ assessment of material condition (NDE).
- Existing plant refurbishment (Repair).
- Similar and dissimilar materials joints (Joining).
- Computer aided development and design of advanced materials and process modelling (Modelling)

Scope

The Energy White Paper published in 2007, "Meeting the Energy Challenge" (1), sets out four challenges for UK energy policy:

- To cut the UK's CO₂ emissions by 60% by 2050, with a 26- 32% cut by 2020 against a 1990 baseline.
- To maintain the reliability of energy supplies.
- To promote competitive markets in the UK and beyond, helping to raise the rate of sustainable economic growth and to improve our productivity.
- To ensure that every home is efficiently, adequately and affordably heated.

The drive to reduce CO_2 emissions in fossil fired power plant requires a twintrack approach. Track 1 requires an approach that will deliver higher efficiency plant whilst track 2 specifically employs technologies to capture CO_2 . Both tracks need to be followed because the energy employed in the capture of CO_2 reduces the overall efficiency of the power plant.

Track 1 invariably imparts higher temperatures on the materials in the boiler and steam turbine, whilst the technologies employed in track 2 such as oxyfiring and solvent extraction impart particularly aggressive high temperature corrosive conditions on the materials used in the capture plant. Materials R&D in both of these areas remains essential for the full scale, long term deploymnent of carbon capture technologies.



Fossil fuel will continue to provide the major contribution to the UK energy over these timescales. It is therefore vital that cost effective fossil-fuelled plant is efficient and reliable in order to contribute to these goals.

Advanced materials provide the enabling technology that allows engineering advances to be implemented. The key to technological advance is the availability of validated materials that enable innovations in design that can be translated into appropriate efficient and reliable plant and hardware. A properly focussed, integrated approach to Materials R&D is vital if the UK is to maintain a leading role in the global power industry.

This report addresses the materials research and development requirements for each of the key fossil fuel generating plant types and associated technologies. In addition brings together the common future research themes where resources and advances can be shared.

The report gives the 'top-level' recommendations for R&D in this area and builds on a comprehensive Technology Status Review (TSR) [ref 2] carried out in 2002 by members of the Materials Group of the Advanced Power Generation Technical Forum. The review, combined with the detail of the individual reports of this MatUK Task Group can be found on the CD attached to this report. There, the reader will find comprehensive technical information and supporting data regarding the R&D requirements for fossil-fuelled power plant.

References: 1. Energy White Paper 2007 2. Review of Status of Advanced Materials for Power Generation, DTI Publication, DTI/Pub URN 02/1267, October 2002

Drivers, challenges and barriers

Energy is essential to every aspect of our life and continued economic prosperity but we face two big challenges: climate change and security of supply.

Today around 72% of the UK electricity needs are met by fossil fuels and they will continue to be the predominant form of energy generation for decades to come [Ref 1]. It is also predicted that the demand for energy will grow from around 350TWh in 2005 to over 400TWh by 2020 [Ref 2]. When this is combined with the closure of existing fossil fired plant to meet EU emission legislation (around 8GW by 2015 - approximately 33% of current capacity) [Ref 3], there is an urgent need for new, low emissions, cost effective fossil power plant. The key drivers for fossil-fuelled energy generating plant are thus to minimise:

- 1 The impact on the environment through reduction of CO_2 emissions.
- 2 Cost (original manufacturer, ownership/use and end of life disposal).

Current estimates are that plant efficiency could be improved by about 15 - 20% over current levels. For a 500MWh coal station equates to a reduction in CO_2 emissions from 0.9Mt/year to 0.74Mt/year (and similarly for an equivalent gas fired station from 0.36Mt/year to 0.29Mt/year) [Ref 3].

For both scenarios, high-efficiency combustion combined with carbon capture and storage increases the reduction to >90% [Ref 3]. Three main approaches can thus be taken to achieve these targets:

- 1 Increasing plant efficiency
- 2 Co-firing with renewable fuels
- 3 CO_2 capture and storage



However these technologies cannot achieve the improved efficiencies without suitable materials, some of which do not yet exist. There is thus a need for to develop new generations and types of materials to meet this challenge.

The key barrier to the long-term development of fossil-fuelled power generation technology lies within the length of the materials development cycle. Time to validation can be up to 12 years. However, industrial, government and academic funding timescales are normally far shorter, up to 3 years. Such timescales are insufficient for development from initial concept through to full-scale production. Success in UK materials development is also limited by a growing shortage of graduates with the necessary skills [Ref 4]. There is a cultural need to excite and attract intelligent and motivated young people into the industry. A subsequent challenge is to ensure that relevant high quality lifetime academic and "on-the-job" industrial training is available.

…innovations in design that can be translated into appropriate efficient and reliable plant and hardware.

References:

(1) Energy White Paper 2007, chapter 5 p92
 (2) Energy White Paper 2007, chapter 5 p93.
 (3) Energy White Paper 2007, chapter 5 p93
 (4) Materials UK IGT People & Skills Report, March 2006

3.0

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In 2006 coal, gas and nuclear power stations generated the majority of the UK's electricity. Thirty large (>1GW) power stations met the majority of electrical demand, which is approximately 40GW but which peaks at 60GW. ⁽¹⁾

72% of this capacity was met by coal (33%) and gas (39%) fired plants. This proportion of fossil fuel generation is predicted to remain approximately constant out to 2020 but the balance will change (1). Around 8GW of the UK's coal power station must close no later than 2015 as a result of EU environmental legislation. Over the next 5 years, around 3GW of gas fired combined cycle gas turbine generating (CCGT) capacity is under construction with an additional 1GW approved and 6GW planned ⁽¹⁾.

Technology status and challenges

In the longer term, the power generating companies wish to build large new coal fired stations to replace the remaining stations and to bridge the growing gap between supply and demand [Ref 1]. Coal and gas fired generating plant is thus central to the future of the UK energy economy and their efficiency will have a significant role to play in controlling UK CO₂ emissions.

However, generating plant is not the only technology that impacts on the CO_2 emissions. The option of combined heat and power production can be adopted to reduce overall CO_2 emissions. Coal gasification and the construction of integrated gasification combined cycle (IGCC) plant offers a further option, and all these fossil fired technologies can potentially be combined with CO_2 capture and storage. The hydrogen economy is also under consideration, but this is outside the scope of this report.

This report therefore concentrates on the generic underpinning technologies and the 5 key areas of fossil fuel power generation:

- Boilers.
- Steam Turbines.
- Gas Turbines.
- Gasifiers.
- CO₂ capture.

4.1 Generic Technologies

There are also 5 key technologies that underpin materials development in all areas discussed in this report. These are:

- Surface protection technologies (coatings)
- Non-destructive evaluation (NDE)
- Lifing
- Repair
- Joining

These must be developed in parallel with the basic materials development programmes in order to reduce development time and to ensure that supporting technology is in place to allow the material to be used in products. Each of these technologies is thus an integral part of the individual materials solution for each component. It is assumed that this holistic systems approach will be adopted.

Improvement in steam plant technology through materials development



References. 1.Parliamentary Office of Science and Technology, Postnote, Feb 2007, No 280

4.2 Boilers

Furnace Walls

Two design approaches for furnace walls are in common use, spiral and vertical. In both designs a welded membrane joins parallel neighbouring tubes. Consequently, weldability and the acceptability of welding without post weld heat treatment (PWHT) become factors in the choice of materials together with strength, corrosion resistance and cost.

In supercritical steam plant operating in the common regime of 250 bar, 540°C, the maximum fluid furnace exit temperature is ~ 420°C. This corresponds to a tube mid-wall temperature some 30°C higher at 450°C at the start of life and a further 10°C higher later in the life cycle due to the insulating effect caused by the growth and deposition of magnetite inside the tube. For a design life of 100,000 hours both 13CrMo44 (1Cr1/2Mo) and 10CrMo910 (21/4Cr1Mo) have adequate creep strength for these conditions but fireside corrosion must also be considered. All boiler manufacturers offer some form of staged combustion to limit NO_x emissions. This requires substoichiometric combustion in the lower portion of the furnace chamber, which produces conditions that can result in rapid thinning and early failure of the membrane wall tubes.

Technology status and challenges

Significant improvements in fireside corrosion resistance are only achieved with much higher chromium levels, >20%. Co-extruded tubing with an austenitic outer layer has been considered but this poses difficulties due to differential thermal expansion and consequential distortion. All boiler manufacturers ensure more oxidising conditions close to the furnace walls through the arrangement of the burners and thus controlled distribution of the flame and its combustion products. Under conditions where this gives inadequate protection consideration can be given to weld overlay or spray coatings to protect the surface.

For the more advanced steam conditions in ultra-supercritical (~325bar and 620 °C) steam plant, two new alloys have been developed from the 21/4Cr1Mo standard. These are 7CrWVNb9-6 (T23) and 7CrMoVTiB10-10 (T24). Both have been designed to avoid the need for PWHT as this can cause difficulties during erection and for in-service repairs.

As steam conditions approach 700°C nickel alloys, e.g. Inconel 740 or Inconel 617, provide the only suitable material solution. These alloys are significantly more expensive than their ferritic counterparts and a significant improvement in boiler efficiency is required to warrant their use. There is thus a clear opportunity for the



development of cost effective new materials instead of Ni-based alloys for these applications.

Superheater Tubes

Superheater tubes are designed to operate at temperatures some 35 to 50°C above the live steam temperature. Current ferritic alloys T91 and T92 are suitable for metal temperatures up to ~615°C. Higher chromium ferritic alloys such as T122 and VM12 have been shown to suffer from precipitation of a deleterious phase (Z phase) with time which reduces their long-term creep strength resulting in allowable stresses not much better than T22.

Fireside corrosion can also be a problem. For example in the 70's CEGB built a plant with final steam temperatures of 565°C and burning coal with chlorine contents around 0.15%. Ferritic alloys were inadequate and re-tubing with austenitic steels of type 316 and type 347 was required. These austenitic alloys have since been modified by addition of copper, boron and nitrogen to improve stress rupture capabilities. Modified thermomechanical treatments have also been used to limit grain size and enhance corrosion resistance. Shot peening of the tube bore has also limited corrosion. Notwithstanding these improvements, the relatively low (18%) chromium content in these steels limits application to ~620°C. For higher metal temperatures austenitic steels NF709 and 310HNbN (HR3C) are available. A recent development (Sanicro 25) exhibits superior stress rupture properties matching the target for austenitic alloys of 100MPa average stress rupture at 700°C for 100,000 hours.

The next stage toward higher temperatures and efficiencies is to move to nickel alloys. Inconel 617 is well proven in German plant but was recognised in the Thermie 700 programme to be incapable of achieving the required average 100MPa-stress rupture at 700°C for 100,000 hours. Special Metals Inconel 740 did however meet this target. This alloy is a variation of Nimonic 263 but with increased chromium and niobium and reduced

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molybdenum to improve fireside corrosion resistance. The precipitation hardened alloy requires a more complex thermal treatment than solution strengthened 617. This is significant in tube bending operations and in developing full strength in weldments. Laboratory testing does not always translate into boiler operation hence 'in plant' testing is required for full component validation.

Fireside corrosion from low-carbon technologies such as oxy-fuel firing requires other materials with properties intermediate between austenitic steels and nickel alloys [e.g. X7NiCrCeNb32-27 (AC66)]. Extensive testing/validation will be needed for these newer materials.

Steam Separating Vessels

Steam separator vessels are often the heaviest walled components in the boiler circuit and are subject to severe thermal fatigue stresses. They separate the saturated steam, which flows on to the superheaters, from water that is returned to the boiler water feed train. Materials such as P11 have proved satisfactory in the past. However, to minimise wall thickness and hence maximise flexibility, materials with higher yield strength are preferred such as 15NiCuMoNb 5-6-4 (WB36) or P91.

Headers and Steam Pipes

Headers and pipework are situated outside the furnace, so fireside corrosion is not a factor in material selection. However, steam oxidation of the bore must still be considered. Early supercritical plant operating around 540-560°C used X20CrMoV121, a nominally 12% Cr martensitic steel, for the highest temperature headers and pipework. Development of P91, a modified 9% chromium steel, enabled higher pressures and temperatures to be accommodated, however the operating temperature was limited to 600 °C due to steam oxidation considerations. Further material developments such as P92 and E911 made possible an increase in metal temperature to ~610°C. Attempts to improve steam oxidation performance through the development of higher chromium

The development of advanced materials can allow reductions in wall thicknesses of main steam pipes. More importantly, they mean the allowable stresses for the same wall thickness can be increased significantly.



(11-12%Cr) variants [P122, NF12 & VM12] led to the formation of Z-phase. Therefore higher steam temperatures with monolithic piping will require more expensive nickel alloys.

9%Cr steel weldments can fail prematurely by "Type IV cracking" in the fine-grained region at the outer edge of the heat affected zone (HAZ). Plant experience demonstrates that this phenomenon is a life-limiting concern, and that changes in design practices are required to achieve adequate long term plant performance. For new

Nimonic 263 extrusion [Courtesy: Doosam Babcock Energy Ltd]

plant designs, an emerging practice is to use nominal design parameters which are substantially more onerous than the actual intended operating conditions, thereby introducing a suitable safety margin, albeit by highly empirical means.

Work is currently underway to restrict or eliminate the Type IV cracking phenomenon. One promising approach is to use higher boron content steels with the aim of eliminating the fine-grained HAZ. However, the need for long term design data is likely to be a barrier to the practical application of improved boron-bearing high alloy steels in the first wave of advanced coal-fired plant planned for construction.

As part of the AD700 programme, the first thick walled pipe in Nimonic 263 at 310mm OD x 66mm wall was produced, with weldability and stress rupture testing currently providing promising results. Further work is ongoing to assess the use of this material in boiler manufacture. Because it is much more expensive than its ferritic counterparts, significant improvements in efficiency need to be realised to make it economically viable.

One method of increasing the service temperature of ferritic alloys is to apply an integral oxidation resistant conversion coating on the bore of the pipe. If this is successful it is hoped that steam temperatures approaching 650°C will be possible.



4.3 Steam Turbine.

High Pressure (HP) and Intermediate Pressure (IP) Cylinders

Material requirements in the HP and IP cylinders depend critically on the steam inlet and reheat temperatures respectively. For the current generation of steam plant these temperatures are up to 620 °C. Inlet temperatures will increase steadily in increments of ~10 °C as the drive for increased efficiency continues. Materials research is required now for plant that will operate at steam inlet temperatures up to 760 °C and above.

Technology status and challenges

Rotor Forgings

Current rotor forgings are based on 9-10% CrMoVNbN steels with either a Mo addition of 1.5% or an addition of up to 1.0%W in partial substitution of the Mo content. V and N contents have been optimised to provide precipitation strengthening through a dispersion of VN particles and a low level of Nb is incorporated to control grain size during high temperature heat treatments. For the very highest temperature applications, additions of boron are being made.

A step-change to the utilisation of Ni-base alloys for rotors is undesirable as it will result in significant cost increases. Consequently the most advanced steels will be pushed as far as possible in order to control costs. Engineering advances, e.g. cooling technology, will be developed in conjunction with alloy development and this may result in a requirement for thermal barrier coatings for the rotor.

A major challenge to the introduction of new rotor materials is their inspectability. As the strength of the material increases, the critical defect size is reduced. A suite of inspection techniques for both surface and submerged techniques is required and the development of this technology must evolve alongside material improvements.

A typical steam turbine rotor installation. [Courtesy: Alstom Power]



Casings and Valve Chest

The properties required from castings for valve chests and cylinder casings are similar to those for rotor forgings. However due to the complex shape castings or multiple forgings are favoured. Therefore the alloys used have additional requirements of good castability or weldability. Similar alloys to those used for rotor forgings are employed but with minor compositional variations e.g. lower C content to provide improved weldability.

A further requirement for utilisation of cast alloys is the availability of appropriate welding processes and consumables. Failure of welded structures at elevated structures usually occurs in the welded region and a 'load reduction factor' concept is frequently used. Measures to improve the properties of weldments either through control of the welding process or through material improvements is a key issue for the development of plant to operate at higher temperatures.

Blading

Blading alloys for operation up to ~600 °C are similar to the rotor forging alloys. However at higher temperatures oxidation becomes an issue. Martensitic steels produce a dilemma in that adding chromium to the alloy to improve oxidation resistance invariably reduces creep strength. Austenitic alloys are currently used successfully by one OEM but as steam inlet temperatures rise to 650 °C and above these alloys again have insufficient oxidation resistance.

The oxidation behaviour of both martensitic and austenitic alloys can be improved by the use of coatings. However for plant operating at >700°C Ni-base alloys will be required to achieve both the strength and oxidation requirements.

Solid particle erosion can be an issue in some turbines and erosionresistant coatings are required to alleviate this problem. These coatings must also be able to meet the oxidation requirements.

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Sealing

Current ring and brush seals of steam turbine power generation plant are limited to operation at temperatures below 550 - 600°. Above this temperature range excessive distortion and wear results in efficiency losses and poor performance that impact upon component design, declared lifetimes and costs of manufacture and operation. The materials requirements for the next generation sealing systems capable of operating at 650°C and beyond are:

- higher temperature creep strength to prevent loss of sealing due to distortion and enable longer lifetimes for components operating under extreme temperatures and pressures
- high temperature resistance to steam oxidation and wear (use of hard facing treatments) providing lubricant-free abrasion resistance and high load bearing capability
- effective use of materials in demanding environments providing reduced costs due to improved design, manufacturing and longer periods between overhaul and applicable to retrofit /upgrade of power generation plant

Valve Internals

The key issues for valves are sliding wear and solid particle erosion. Abrasion-resistant coatings or welded inserts are used on a regular basis in current plant as a palliative measure. As the steam temperature increases these components will be subjected to more aggressive conditions and it is envisaged that the erosion/corrosion resistance of valve internals will be a key issue in future steam turbine development.

Bolting

Meeting the requirements of bolts operating at the very highest temperatures has frequently required exploitation of Ni-based alloys such as Nimonic 80A or Refractalloy 26. Even higher strength alloys will be required for >700°C.

Several Ni-base alloys have an inherent problem in that they undergo a lattice transformation during prolonged exposure to a specific temperature range. This results in contraction of the material and overstressing of the bolt. Alloys need to be identified that have sufficient resistance to stress relaxation and also do not undergo this transformation.

Low Pressure (LP) Cylinder

Material requirements for the LP cylinder are primarily dictated by the need to avoid stress corrosion cracking (SCC) and fatigue. Steam entry and exit temperatures are typically 250°C and 40°C respectively.

Rotor Forgings

LP rotors are usually manufactured from low alloy NiCrMoV steel. Designs may be either monobloc or welded construction. A key requirement is to avoid SCC in blade attachment areas. However as a material's strength increases so does its susceptibility to SCC. Design approaches that have been implemented include the use of welded rotors to use material of an appropriate strength in areas where an environment conducive to SCC is present. The use of welded rotors introduces a requirement for inspectibility which must be addressed in a similar manner as for HP rotors.

An alternative approach to avoiding SCC in rotors is the use of local surface treatment to introduce compressive residual stresses in critical areas. Work is required to optimise these processes to develop a suitable residual stress profile without damaging the alloy surface.

Casings

Casings are not generally highly stressed. Carbon steel or cast iron is usually used subject to flow accelerated corrosion resistance being acceptable. No major issues are anticipated and research requirements are minimal.

Blading

Blading requirements vary along the steam flow of the LP turbine. Blades near the inlet are relatively small and operate in "dry" steam. Near the outlet the blades are much longer and operate in steam that contains significant moisture. Precipitation hardened stainless steels are usually used for the longest blades although titanium alloys have acceptable properties (albeit much higher cost).

Efficiency improvements can be achieved through the use of longer last stage blades. This requires alloys with higher specific strength than those currently used but also having adequate SCC resistance. Alloy development, both of steels or titanium alloys, is required to achieve this balance of properties.

Last stage blades are also subject to water droplet erosion. For current alloys the leading edge of the blades may be modified for increased erosion resistance through cladding, welded inserts or local hardening. Any new alloy introduced for last stage blades must either have intrinsic resistance to water droplet erosion or be amenable to modification to achieve the desired level.

4.4 Gas Turbines.

Compressors

Future compressors need to provide improved cycle efficiency, operability and reduced costs by optimising the work done by each stage. This can be achieved by better control of the pressure ratio and mass flow through the compressor, improved component reliability and reduced parts count. As well as the materials developments advanced manufacturing methods are being introduced to enable cost reduction and improved integrity. For example, welded structures are being considered to replace bolted joints.

Future developments are aimed at increasing pressure ratios from the current 15:1 level to 40:1 and beyond. The need to maintain compressor performance and integrity through life, while reducing parts costs and the use of more effective manufacturing processes is paramount, as is the need to achieve operational lifetimes in excess of 100,000 hours. Many of these targets are dependent upon improved design and aero-thermal analysis methods in conjunction with test and validation procedures; however without suitable high temperature materials these cannot be achieved.

For small to intermediate gas turbine compressors, temperature loadings currently range from -50 to about 500 °C. In the short to medium term the continued use of improved low-

Technology status and challenges

The development of disruptive technologies is essential if efficiency increases in turbines are to be maintained. The current materials are being pushed to their mechanical and physical limits in terms of both strength and temperature capabilities. Higher temperature materials allow for reduced cooling air

requirements and hence higher efficiencies. Designing with 'novel' materials must take into account key issues such as manufacturability, quality, inspection and re-use.



alloy and ferritic stainless steels will be adequate. However eventually aero-derivative titanium alloys, nickel alloys and composites will be employed. This would present a significant increase in cost and manufacturing complexity (forgings, machining, joining, component lifing) as well as operational difficulties (component handling, overhaul, repair, cleaning) and may introduce additional problems associated with thermal mismatch and fretting fatigue from adjoining ferritic alloys.

Issues associated with rotor corrosion are largely operator dependent, being influenced by the specific nature of

Siemens SGT 400 gas turbine [Courtesy: Siemens Industrial Turbo Machinery]



the fuel, compressor washing and cleaning practices. These are currently addressed by use of protective coatings. Likewise, abradable tip seal coatings are currently used to provide and maintain efficiency and currently present little technical risk.

For large utility power generation engines, performance is currently limited by the temperature and strength capability of the rotor steels used. Development and demonstration of high-nitrogen, nano-precipitate strengthened steels for high pressure compressor disc applications could offer equivalent strength and temperature capabilities to some nickel based alloys with much reduced cost. Application of these high strength creep-resistant steels necessitates the development of improved large-scale melting (up to 100 tonnes) and forging capabilities (up to 18 tonnes) and the development of suitable welding technologies, non-destructive testing methods for large-scale rotors and validated life assessment and risk analysis methods. Successful development of these technologies would negate the need to introduce more expensive (by a factor of 5) nickel alloy technologies. Materials and process developments will be heavily dependent upon successful integrated process modelling that links process developments to materials performance and enables

optimised, affordable, manufacturing routes to be developed.

An added complication for the compressor is the introduction of water/fogging at the intake to improve performance. The presence of water droplets leads to erosion issues on compressor blading. In the short term this will be mitigated through the development of erosionresistant coatings for existing materials but in the longer term an erosion-resistant materials system solution will be required.

Combustors

The combustor experiences the highest gas temperatures in a gas turbine and is subject to a combination of creep, pressure loading, high cycle and thermal fatigue. The materials used presently are generally wrought, sheet-formed nickel-based superalloys. These provide good thermo-mechanical fatigue; creep and oxidation resistance for static parts and are formable to fairly complex shapes such as combustor barrels and transition ducts. Equally of importance is their weldability, enabling design flexibility and the potential for successive repair and overhaul operations, which is crucial to reducing life cycle costs. The high thermal loadings imposed often mean that large portions of the combustor hardware need to be protected using thermal barrier coatings.

Current temperature loadings experienced by combustors range from 1250 to 1375°C, depending on engine size and duty cycle. Future developments aim to reduce CO_{2} , NO_X and SO₂ emissions to meet environmental legislation. Customer demands for cleaner running by optimising the distribution of fuel during firing and by using catalytic combustion systems. This will place a limit on the future turbine entry temperature levels and will require control of peak flame temperatures within the combustor. This should also provide more air for cooling the combustor liner; however, other components may be required to run hotter as the demand for combustion flame temperature control increases.



Rolls-Royce RB211 dry low emission industrial gas turbine. [Courtesy: Rolls Royce plc]

Materials technology acquisition programmes for future combustor designs are aimed at replacement of conventional wrought nickel-based products with:

- Higher performance Ni-based alloys.
- Ceramic matrix composites.

The programmes are primarily aimed at addressing the limitation in temperature capability and coating compatibility of current alloys. Candidate materials have been identified and demonstration hardware has been manufactured and engine tested. However, there are limitations to these technologies that need to be overcome before they can be deployed on products, e.g. joining methods, environmental barrier coating systems, robust design, inspection, lifing and repair capabilities. These materials have also been identified as candidates for efficient, high temperature heat exchangers for a range of externally fired combined cycle systems that separate the turbine working fluid from the aggressive combustion gases generated by poor quality fuels. This limits the damage incurred by hot section hardware during engine running and enables the use of a range of low calorific value and biomass fuels with combined heat and power recovery systems.

Oxide dispersion strengthened metallic systems have also been considered in these applications but there is no current commercial producer of these materials. As a result these are not considered viable materials until this situation changes.

The current thermal barrier coatings technology for metallic combustor applications is based exclusively on multi-layered systems comprising of a MCrAlY bondcoat and a ceramic topcoat applied using plasma spray deposition techniques. Application of this technology generally aims to limit peak metal temperatures between 900 and 950°C. Future developments are aimed at applying thicker coatings to enable higher flame temperatures and/or reduce metal temperatures further. Other programmes are aimed at increasing the phase stability and resistance to sintering of the ceramic topcoat at temperatures above 1250°C and to the inclusion of diagnostic sensor layers within the coating that enable the plant and component condition to be actively monitored. New materials will however require new coatings systems that can only be specified and developed in parallel with the substrate development.

Turbine blades

Turbine blades are subjected to significant rotational and gas bending stresses at extremely high temperatures. In addition to normal start-up and shutdown operation unexpected interruptions and shutdowns introduce severe thermomechanical loading cycles. The turbine entry temperature is typically in excess of 1375°C, with base metal temperatures ranging from 700 to >1050°C. The target lifetime under these conditions is dependent on engine type and duty cycle, but can be in excess of 50,000 operating hours. The blades pass through the wake of the combustor and nozzles and are subject to high frequency excitations, which can lead to high cycle fatigue failure. The highpressure stages are cooled to withstand the hot gas temperatures and coated to restrict corrosion and erosion of the blade structure.

For many years the primary consideration in the design of blades has been to avoid the possibility of creep failure. To meet this requirement, and increase the efficiency by running a higher turbine temperatures, more advanced materials have been continuously introduced. For vanes and blades there has been a gradual move away from conventionally cast nickel-based superalloys towards directional solidification and single crystals. The increased cost of manufacture is mitigated by the use of recycled materials and increased casting yields, and offset against improved component lifetimes and more efficient running (through the higher turbine entry temperatures they make possible). Alloys with greater defect tolerance to low and medium angle boundaries need to be developed and validated with advanced modelling of the behaviour of defects under load. Equally there is a need to develop alloys which are less susceptible to microstructural and mechanical property degradation.

To achieve increased creep strength, successively higher levels of alloving additions have been used to increase the level of precipitate and substitutional strengthening. However, as the level of alloying has

Technology status and challenges

increased, chromium levels have had had to be significantly reduced to offset the increased tendency to form deleterious phases, which limit ductility and reduce strength. Reduced chromium levels also significantly reduce the corrosion resistance of the alloys. This has necessitated the development of a series of protective coating systems. Although the coatings are intended to increase component lifetimes, but they often demonstrate low strainto-failure properties that can impact upon the thermo-mechanical fatigue endurance.

The development of blade alloys specific to industrial gas turbines continues to be a difficult problem to resolve. Much dependence has been placed by the land-based sector on the transfer of advanced technologies from the aero sector but this has not always provided the necessary solutions.

A number of alloys having improved castability, higher corrosion resistance and reduced heat treatment times have been developed, but with limited success. Future emphasis should be on a total system that addresses alloy development, coating, lifing and repair as an entity rather than as a series of unrelated steps. This holistic approach will be critical to the

Increases in

gas turbine

turbine to

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success of future for all gas and steam turbine materials and process development. There is also further scope in industrial gas turbines for continued incremental development of Ni-based alloys and coatings for the short and medium term.

Turbine Discs

The main functions of a turbine disc are to locate the rotor blades within the hot gas path and to transmit the power generated to the drive shaft. To avoid excessive wear, vibration and poor efficiency this must be achieved with great accuracy, whilst withstanding the thermal, vibrational and centrifugal stresses imposed during operation, as well as axial loadings arising from the blade set. Under steady-state conditions, current turbine disc temperatures can vary from approximately 450°C in the hub to in excess of 650°C close to the rim with a requirement for >50,000 hours operating life. These temperature loadings are set to increase further across the disc as the demand for improved efficiencies continues.

Creep and low cycle fatigue resistance are the principal properties controlling turbine disc life and to meet the operational parameters requires high integrity advanced



Trends in GT temperatures through materials development

of advanced materials and processes from conventionally cast nickel and cobalt based alloys through to single crystal alloys. This combined with developments in thermal barrier coatings and advanced cooling technologies have seen firing temperatures almost double in the last 50 years.

materials. To meet the highest operating temperatures and the component stress levels demanded, it has been necessary to develop a series of progressively higher strength steel and Ni-based superalloys. These are generally manufactured using cast and wrought processing. However, the complex chemistry of these alloys makes production of segregation-free ingots very difficult. Manufacture of larger components, or more complex alloys, would necessitate a change to atomised powder processing to limit segregation, while dual alloy processing offers the potential for overcoming the variability in strain distribution across the section of large forged turbine wheels. Many of these developments are being pursued by the aero-gas turbine industry to meet their more demanding conditions. It is assumed that much of this aero-derived technology can be inserted into energy generating applications. However cost may preclude this, in which case a new approach to the materials, design, manufacture and repair of such components aimed specifically at energy requirements will be required.

The issue of coatings development for turbine discs is currently treated in the same way as coating for blades but is a much less mature technology. The same holistic systems approach is therefore required.

Sealing

Turbine gas path seals include rotor tip seals and disc rim seals. On unshrouded rotor tips and rim seals, coatings such as MCrAlY and Nickel-Graphite can be employed as an abradable coating to avoid damage in the event of a rub. Erosion resistance and the ability to provide abradability after long-term exposure at high temperature are required for such coatings. On shrouded rotor blading, superalloy honeycomb foil materials are employed as abradable seals and high temperature oxidation resistance is needed for foil materials to achieve long life at high temperature. Research is ongoing to develop improved seal materials and novel methods of construction and application for the above seal types.



The labyrinth seal is the most common form of air system seal, usually with an abradable stator material. Positive contact carbon seals are often used for bearing chamber seals. The development of brush seals has provided improved sealing efficiency and is displacing the use of labyrinth seals in critical locations. Both metallic and nonmetallic bristles are employed depending on temperature levels and the key requirements for wear and fatigue resistance. Film riding face seals have the potential for even higher sealing efficiencies but place extreme demands on manufacturing technology.

Static seals are used to seal gaps and joints between components where

there are small relative movements due to thermal expansions and they can be employed on both turbine rotor and turbine and combustor stator components. On cylindrical joints, piston rings and E seals are used and for sealing gaps between adjacent blades and vanes strip seals are employed. On rotor blades it is common for sealing features and blade locking features to be combined. Seal strips and E seals used in high temperature locations employ wrought sheet materials as used for combustor components. Wear and fretting can be experienced on such seals and the development of hard coating systems can alleviate this. Brush seals, used in a static application, can allow larger thermal movements with low leakage.

4.5 Gasifiers

Materials issues in the major gasification process components are mostly restricted to the gasifier vessel, downstream coolers and gas cleaning vessels, and the gas turbine where the fuel is burned.

Refractory Lined Gasifiers

During the gasification process the chamber typically operates at temperatures between 1250 and 1550°C, and at pressures of 3 MPa or higher, and so it is usually lined with refractory materials to contain the severe environment and to protect the outer steel shell from erosion, corrosion, and the high temperatures. In addition to the lining, the gasifier is usually cooled by air or by water.

Water cooled gasifiers typically have a working face lining of Al_2O_3 -SiC refractory, and have a satisfactory service life because slag freezes on the refractory surface, restricting slag penetration and corrosion. Air cooled gasifiers are also lined with refractory materials - a typical liner would be a high chromium oxide material that contains alumina and may contain other additives like zirconia. The liners can last from between three months to two years.

Different commercial gasifiers

Technology status and challenges

The major challenge for gasifier refractory materials is for them to provide an adequate period of protection to the gasifier structure. Generally, industrial applications run two gasifier units, so that one can continue operation whilst the other is being refurbished. Therefore the lifetime of the lining should be predictable so that outages can be planned.

A suitable refractory requires the following characteristics:

- Endurance at elevated temperatures
- Ability to accommodate thermal shock from temperature transients
- Resistance to erosion by particulates
- Molten slag resistance
- Resistance to corrosive attack from hot gases of varying composition
- Ability to withstand variable oxidising and/or reducing conditions.

Historically a number of refractory compositions have been evaluated for use in these harsh thermal environments. They include:

- Sintered and/or fused cast alumina-silicate
- High alumina, chromia-alumina and chromia-magnesia spinels
- Alumina/magnesia, alumina and chromia
- Silicon carbide (SiC) refractory compositions.



Each composition has its particular benefits and disadvantages, e.g.

- Fuse-cast refractory materials with little or no porosity have good chemical wear resistance but poor resistance to thermal shock.
- Materials containing high levels of Al₂O₃ or MgO/Al₂O₃ spinel have very poor wear resistance, as do refractories containing SiC and Si3N4.
- As a general rule, additions of chromium oxide to a refractory composition tend to improve resistance to chemical attack from slag.
- Refractories with high chromium oxide content (>85 wt% Cr₂O₃) are used in severe wear areas of a gasifier, whilst lower chrome oxide materials are used in less severe wear areas. A minimum Cr₂O₃ level of 75wt% is thought necessary for sustained material performance in slagging gasifiers.
- Refractory compositions suitable for economic operation in aggressive gasifier environments are: Cr₂O₃/Al₂O₃, Cr₂O₃/Al₂O₃/CrO₂, and Cr₂O₃/MgO.

High chromium oxide refractory materials have evolved as the material of choice to line the hot face of gasifiers but the performance of these materials does not fully meet the desired service requirements of industry. Future developments will include:

- Development of refractory material coatings
- Monolithic linings
- Refractory materials that do not contain, or are low in, chromium oxide.

Research is currently underway in the US to move away entirely from chromium oxide refractories because of cost, health and environmental/processing issues.

It is clear that high Cr₂O₃ refractories fail to meet the performance requirements of gasifiers. An alternative refractory based on alkali-aluminate has been developed and is under evaluation.

Gas Coolers

Once generated, the gases need to be cooled and cleaned before being burnt in the gas turbine. The raw hot gas is mainly carbon monoxide (CO) and hydrogen (H₂) with hydrogen sulphide (H₂S) as the major corrosive impurity. The gas mixture is cooled and water quenched to remove particulates and water-soluble impurities such as ammonia (NH₃) and chlorides. The heat exchanger that cools the raw fuel gas is the first major component downstream of the gasifier vessel. Gas coolers can be either 'water-tube' or 'shell-boiler' in type. Cost is a key issue in gasification systems; hence most current systems use the cheaper shell-boiler approach, which is suitable for modest steam conditions but increases the risk of fouling and blockages of the gas stream.

The presence of ash/char particles can cause erosion, abrasion or deposition in the gas cooler, leading to blockages, while gaseous species cause corrosion and further deposition through condensation of vapour-phase species such as alkali and trace metal chlorides/sulphides.

High temperature corrosion in 'syngas coolers' is unique to gasifiers, especially when coal is used as the fuel. At present heat exchanger syngas operating temperatures are generally less than 450°C. This is partly due to concerns over high temperature corrosion and partly because the use of higher heat exchanger temperatures is not deemed cost effective.

One of the critical high temperature corrosion mechanisms in gas coolers is sulphidation. In carbon and lowalloy steels the rate of attack is too high to allow the use of these low cost materials. Alloy 800 has adequate properties at an economic price and is generally used. However, the sulphidation potential is not the only parameter to affect the corrosion rate of candidate materials; corrosion rates also depend on the chloride content of the gas. Alloys with relatively low chromium content, such as Alloy 800 and its weld material Inco 82, are particularly susceptible to corrosion whilst high chromium materials

with additional alloying additions such as aluminium (Al) and silicon (Si) are less affected by the presence of HCl. 310 stainless steel has an adequate corrosion resistance but is not currently approved due to waterside corrosion issues. Sanicro 28 is currently the favoured material.

Aqueous corrosion during downtime will further increase corrosion rates of materials; this is particularly problematic in the presence of chloride-containing deposits. During downtime, chlorides penetrate through cracks in the oxide scale and attack the metal at the oxide/metal interface. Iron chlorides formed by this attack then cause spallation of the oxide scale during start-up, exposing fresh metal for further corrosive attack. In the absence of this spallation, stainless steels, with more than 20 wt%Cr are adequate for gas coolers working between 300 and 400°C. Where spallation occurs, the corrosion rate of stainless steels is too great and molybdenum containing materials, such as Sanicro 28, offer better protection. If the gas also contains high levels of chlorides, stainless steels are unacceptable, and so Alloy 625, containing molybdenum and a high level of nickel, is the preferred material.

One of the biggest challenges in gasification systems lies in the development of a reliable and economically viable cooling/cleaning path. This will require R&D for syngas coolers that is centred on development of alloys and manufacturing processes to improve corrosion resistance and lower the cost of these components. The development of improved hot gas clean-up systems could lower the cost of IGCC by providing a cheaper alternative to the conventional low temperature processes currently used.

Gas Turbines

Although gasification plants use multiple stage clean-up processes for the syngas, a limited amount of impurities do enter into the gas turbine hot section flow path after the combustion process. This leads to a risk of damage to the vanes and blades of the turbine. Given the inherent variability of feedstock into the gasification process the composition of impurities varies greatly making it more problematic for materials than conventional gas turbines.

In general the issues found in conventional gas turbines (see section 4.2) can be applied to syngas-fired turbines with the added complexity of the fuel and impurities. At present syngas-fired turbines are operating at similar firing temperatures as natural gas turbines. This is due to the increase in mass flow through the turbine of around 14% compared to natural gas. Whilst this does produce higher turbine outputs it also generates greater heat transfer to the hot section vanes and blades. Hence there is likely in future to be a need for higher temperature materials. Control of NO_X may also cause problems, as water (either used as a dilutant or produced as a by-product) will increase degradation of hot section components. Greater understanding of the effect of water on the oxidation of materials needs addressing. It is likely that the gas inlet temperature of the turbine will be increased in future to meet efficiency goals. Whilst this will affect the use of high temperature alloys it will also exaggerate the effect of molten salts and deposits. It has been shown that very low levels of gas stream ash and impurities can produce substantial degradation through corrosion, deposition and erosion.

Limited plant experience substantiates the problem associated with deposits and erosion; hot section coatings, vanes and blades frequently need replacing during maintenance periods. It is also worth noting that shutdowns are more frequent with syngas turbines so materials that are more resistant to cycling and improved gas cleaning will be a requirement. It has been suggested that there is a critical transition temperature where corrosion and deposition rates increase dramatically. Hence whilst raising inlet temperatures will improve overall efficiency but it could also cause greater degradation. Research into control of this critical transition temperature is essential to the future success and uptake of this technology.

4.6 CO₂ Capture

There are a range of technologies under investigation for the capture of CO_2 from energy and other industrial processes. These are usually classified as:

- Post combustion where the CO₂ is separated from the process gas stream downstream of the main process components and after any fuel content has been burned. This approach can also be adopted in a similar way for other industrial process with high CO₂ emissions, e.g. cement production, steel production, etc.
- Pre-combustion, where the carbonbearing compounds are removed from the gas stream prior to the combustion of the fuel constituents, and
- Oxy-fuel, where the fuel is burned in an enriched oxygen content gas resulting in an exit gas which has high levels of carbon dioxide and steam which are readily separated by a condensation step.
- CO₂ transport.

Technology status and challenges

Post Combustion Capture

A number of technology options exist for capturing CO_2 downstream of the combustion of a fossil or biomass/waste fuel, in both new plant and retrofit applications. The basic approach is illustrated in the diagram below.

Low temperature liquid scrubbing, using amine-based solvents, is the most likely technology to be deployed in a first generation system. Such scrubbing technology has been widely used in the oil/gas sector for separation of CO_2 from natural gas, but to date there are few demonstrations of its application in large-scale power plants. Oxygenbearing flue gases with a range of contaminants also pose performance and durability problems not experienced in natural gas systems.

An amine scrubber comprises two separate units:

- * An absorber where CO_2 -lean solvent reacts with flue gas CO_2 at temperatures typically between 40 and 60°C.
- * A stripper (or regenerator) where CO₂-rich solvent is heated to 100-140°C with steam to strip the gas at close to atmospheric pressure.

Amine-based solvents have been enhanced over the years and a range of variants is available from different suppliers. Many include proprietary additives to improve performance/other characteristics.

Existing 'industry-standard' solvents were developed to remove acid gases from natural and synthesis gas streams and so are not necessarily suited for the removal of CO₂ from flue gases. For oxygen-containing flue gases from power plants, where CO₂ concentrations are low, high CO₂ capacity/reaction rates and low heat of desorption energy are essential, as well as low by-product formation and durability in service.

In any power plant system, the performance, reliability and availability of all system components are critically important to economic viability. Outside the providers of amine scrubbing equipment, there is little knowledge of the issues affecting the durability of the solvents or the structural characteristics of the scrubbers.





Critical materials issues in amine scrubbing are:

- Corrosion resistance in scrubber environments (including performance of carbon- steel, various grades of stainless steel, ceramics and plastics)
- The performance of corrosion inhibitors
- Potential surface treatments and coatings which could offer protection and/or repair options
- Assessment of whether there are critical fluid velocities above which erosion-corrosion becomes significant
- The lack of knowledge of corrosion mechanisms that may occur in service (e.g. pitting, localised corrosion at welds, stress corrosion cracking, etc.)
- The effects of different amine solvents, amine concentrations and degradation products on corrosion
- The performance of materials for valve stem packing, pump seals, plate heat exchanger gaskets, etc.

Alternative post-combustion CO_2 separation approaches include the use of ammonia, solid sorbents (e.g. lime or alkali compounds), adsorption on molecular sieves or active carbons (using pressure, temperature or electrical swing systems) or cryogenics. All present materials challenges when their implementation in operational plants is considered.

Pre-combustion Capture

Advanced gasification systems are being developed for the generation of power using chemical feedstock, liquid fuels and hydrogen, the latter option requiring the use of a CO₂ capture process. High pressure, oxygen-blown gasifiers are the most suitable for use with CO₂ capture. To enable CO_2 to be captured, the fuel gas (pre-combustion) has to be fed to a catalytic shift reactor where most of the CO is reacted with steam to give H₂ and CO₂. Steam has to be taken from the steam cycle and added to the fuel gas feed to the shift converter, which will affect the efficiency penalty for CO₂ capture.

The fact that the CO_2 is relatively concentrated in the shifted fuel gas (around 50 vol%) and at high pressure, presents an opportunity for lower cost CO_2 capture compared to pulverised fuel plants where flue gas are at atmospheric pressure with CO_2 concentrations of 10-15% (vol). A number of approaches can be used to separate CO_2 from the shifted fuel gas. Variants include:

- Use of physical solvents e.g. the Rectisol process (using cold methanol)
- Selexol process (using a dimethyl ether of polyethylene glycol etc.)
- Solid sorbents or adsorbents
- Cryogenics
- Advanced separation membranes

The physical solvent approach is well established for ammonia production plants but has a relatively high efficiency penalty, whereas membranes can be tuned to plant conditions and so offer the lowest efficiency penalty.



There are many research initiatives around the world investigating separation technologies, although only limited activities have taken place in the UK in recent years. In particular, development of membrane-based options for separation of the H_2/CO_2 stream should be encouraged alongside development of membranes for the separation of oxygen from air, in order to reduce the cost of oxygen for these energy systems.

Membranes based on polymers, metal (Pd/Ag) and ceramic have been evaluated and all have potential opportunities. The preferred membrane system should have high selectivity for H_2 as well as a high flow capability, as power plants will provide immense gas flows. Previous studies have highlighted the large size of the membrane separator plant compared to the power plant itself.

Technology status and challenges

Oxy-Combustion

Combustion of fossil fuels in an oxygen-enriched/low nitrogen environment leads to the gaseous combustion products being mostly a mix of CO₂ and steam, which can readily be separated using a condenser, leaving a high concentration CO₂ stream for further clean-up, compression, transportation and storage. This approach can be used with coal in pulverised fuel boilers. The nitrogen in the air which would previously have been the oxidant is replaced by recycled flue gas (i.e. mostly CO₂ and steam).

Oxy-combustion is of major interest in the UK as it can be deployed in existing and new pulverised fuel plants using advanced steam conditions. The materials challenges are centred on the changes to the boiler environment as a result of the flue gas recycle, although other parts of the systems, such as the steam condenser/CO₂ separator, could also provide unexpected materials problems in service.

In pulverised fuel boilers, the combustion chamber environment will contain significantly higher levels of CO₂ and steam than in conventional air-firing, along with much higher levels of contaminants such as SO_x ; up to 5 times conventional levels depending on where the recycled flue gas is taken from. The cleanest, though most expensive option is to recycle after the flue gas desulphurisation system, thus reducing the levels of SO_x in the boiler but increasing the size of the FGD plant to handle the full flow of cycling flue gas.

By comparison, the cheapest option is to recycle to flue gas with little pre-cleaning (maybe after some particle removal) giving the dirtiest/highest SO_x flue gas. Other contaminants and particulates will also be recycled and as a result can lead to increased fouling and corrosion, at significantly higher levels than experienced in the past. Water-wall and superheater corrosion are a major research area for such systems, particularly when combined with advanced supercritical plant conditions leading to higher levels of contaminants and temperatures.





Oxy-combustion is also a major interest in fluidised bed systems where the ability to control combustion conditions with a minimum of flue gas recycle means that plant sizes can be significantly reduced thus reducing capital costs.

Research has been carried out into oxy-combustion in the UK, but more work is needed to understand the changes to the process environments and to develop robust approaches to avoid unforeseen service problems.

Advanced cycles, often using elements of the oxy-combustion approach are also in the developmental stages. Examples include lime-based post-combustion capture where oxy-firing is used for the calcination step, or chemical looping where the oxygen is provided from a solid oxide.

CO₂ Transport

CO₂ captured using the technologies described earlier will be impure and will contain various other gases depending the type of power plant and the capture technology used. The CO₂ will contain contaminants such as SO_x, HCl, NO_x, as well as trace metal compounds due to inefficiencies of the current gas cleaning technologies. Such contaminants may be deliberately left in the CO₂ stream if their storage with the CO₂ proves acceptable to the regulatory authorities. If not, further gas cleaning stages will be necessary. 'Contaminated' CO₂ provides a potentially aggressive environment for the pipeline or other transport system to the storage location, which for the UK is expected to be under the North Sea.

While pipelines are used currently to transport CO₂ it is unlikely that capture technologies will be unable to deliver a CO₂ stream which would consistently meet the current specification for CO₂ transport (>95% CO₂, <4%N₂, no free water, <1450ppm total S, <10ppm O₂, etc). Special clean-up measures would be needed, which may deliver additional species, which are currently not specified. Little research has been carried out into this issue and more work needs to done if reliable CO₂ transport systems are to be provided at affordable cost in the near term.



The UK remains a centre for technical excellence in fossil energy materials, particularly high temperature materials and coatings. By working with the funding agencies, academia and industry we can enhance this expertise to remain at the forefront of future materials technologies.

5.1 Current Materials R&D Programmes

Materials development is a long term process. A typical materials development programme proceeds through several stages:

- Investigation of trial melts including testing to at least 15,000 hours (~2 years) before selection of the most promising new compositions
- Manufacture of a prototype component in the best trial melt (~1 year) to demonstrate that the alloy can be applied to the appropriate, sometimes very large, components without problems arising from excessive segregation or cracking during manufacture. Inspectability of large components also needs to be demonstrated.

Materials research & development

- Characterisation of the prototype including testing to at least 30,000 hours (~4 years). There is potential for significant variation of properties through the section of large components, especially in comparison to the properties achieved in trial melts.
- Launch as commercial material (~1 year);
- Test commercial products to establish scatterband of properties (~4 years). Cast to cast variation in properties is typically of the order of +/-20%. Knowledge of this scatterband and the position of the first prototype within it is required to fully exploit the properties demonstrated in a single prototype.

It typically takes 12 - 15 years to achieve a completely reliable, validated material. Timescales for implementation of novel process cycles may be even longer.

Since many of the industrial gas turbine (IGT) materials are derived from aero-engine applications, few specific IGT materials programmes are active in this sector. Current research activities described below must therefore be regarded within this context.

UK Research

UK government supports several boiler and steam turbine activities. Current projects include:

- Alloy Development For Critical Components On Future Coal-Fired Power Plant
- High Temperature Sealing for Advanced Super Critical Steam Turbine Plant
- Advanced Materials For Low Pressure (LP) Steam Turbines
- Improved Modelling of Materials for Higher Efficiency Power Plant

The Department for Business, Enterprise and Regulatory Reform (BERR) also funds UK participants in a project allowing collaboration between UK and US organisations. Activities include steam oxidation and microstructural degradation of alloys used in boilers, steam turbines, and gas turbine materials.

The National Measurement System Materials Programme has a rolling programme that includes projects, carried out at the National Physical Laboratory, which support materials for fossil fuelled power generation: Two current projects are, 'Key measurements on in-situ oxide scales to ensure future energy security' and 'State of the art diagnostic measurement for lifetime management of critical parts in efficient energy generation'. These projects began in April 2007 and are planned to run for three years. There is potential for new projects relevant to fossil fuelled power generation to be launched in future years.

The Engineering and Physical Sciences Research Councils Supergen II Programme on conventional Power Plant Life Extension, funds work, with additional support from an industrial consortium, at four UK Universities. This programme includes tasks on Condition Monitoring, Microstructural Degradation and Modelling of Mechanical Behaviour and covers boilers, steam and gas turbines. Outside of this, the situation on work on Gas Turbine Materials is the same as in Europe, very company specific, addressing their own individual problems and largely aero derived.

Little work is underway on Materials for CO_2 capture and bulk CO_2 transport.

Materials development is a long term process... ...it takes 12-15 years to achieve a completely reiable and validated material \$\$

Materials research & development

European Research

Companies, universities and research institutes are active in a number of major EU projects for development of boiler and steam turbine materials. The COST 536 programme covers a wide range of power generation technologies and includes most European boiler and steam turbine makers and their materials suppliers. The programme started in 2004 and runs to 2009. UK participants are supported via the Technology Strategy Board's Technology Programme. The main objective of COST 536 is the development of materials technology to enable operation of power plants with steam temperatures of 650°C.

A parallel programme, COST 538, focuses on Plant Life Extension. The programme includes materials and coatings for steam turbines, gas turbines and boilers and is improving understanding of degradation mechanisms in high temperature materials.

In the EU AD700 project, launched in 1998, the first three years resulted in confirmation of the technical and economic feasibility of the concept, which fundamentally depends on the application of nickel-based alloys in steam turbine parts to enable steam temperatures of 700-720 °C. The application of Ni-based superalloys at steam temperatures up to 700°C/375 bar will give an overall thermal efficiency of up to 55%,

[Courtesy: Alstom Power]



compared with the 47% efficiency of state of the art 600°C/300 bar/300 bar double reheat plant. This is expected to reduce fuel consumption and thus CO₂ emissions by around 15%. Much larger components are required for steam cycle plant than for gas turbines so these temperature increases represent a significant materials challenge. Turbine-related activities included the assessment of a range of candidate alloys and the manufacture of the first prototype components. The second phase, which was completed at the end of 2006, included the extension of the prototype demonstration and characterisation programme. The success of the AD700 project encouraged the launch of a demonstration programme involving the operation of critical boiler and turbine valve components in an operating power station in Germany. This COMTES 700 project is supported by a consortium of European utilities and by the EC. The demonstration components have been successfully operating at 700°C since July 2005. A number of programmes are being considered under Framework 7 funding in the area of energy materials on similar topics to the above but as yet none have been launched.

In Germany there is strong national funding for the COORETEC and MARCKO programmes, and the VGB is funding the long-term characterisation of advanced 9-12%Cr steel components.

Whilst the general aims of the EC and other collaborative programmes on nickel-based alloy steam plant has been a long-term development, one company, E.ON, has stated its intention to make an imminent start on the design and construction of a full scale demonstrator plant.

There are relatively few industrial Gas Turbine Materials collaborative programmes within the EU, those that exist tend to be based on a single company and its supply chain addressing their own specific needs. There is little evidence of the large pan European and National programmes seen in Boiler and Steam turbine areas. It is difficult to gauge the level of R&D that is currently active, especially given the



complication of the aero derivative nature of many of the Materials.

Little work is underway in the areas of Materials for CO_2 capture and bulk CO_2 transport.

Research in Japan

In Japan the National Institute for Materials Science (NIMS) is responsible for major high temperature materials programmes. The major steels programmes have focused on the continued development of 9-12%Cr steels for 650°C steam conditions, the same principal objective as COST 536. In addition a feasibility programme funded by the Electric Power Development Corporation to develop was 700°C steam conditions was carried out in 2000-2002 and in 2006 the Ministry of Economy, Trade and Industry (METI) and the New Energy and Technology Development Corporation (NEDO) launched a materials development project with objectives of up to 800°C.

NIMS has a continuing activity to develop novel compositions for single crystal Ni-base superalloys for gas turbine blade applications and forged alloys for gas turbine discs with properties equivalent or superior to powder processed materials, however this work is largely aimed at aerospace applications.

For future improvement in power generation efficiency NIMS foresee closer collaboration between materials research and engine design research and greater use of locally produced materials.

There appears to be little work on CO_2 transport and storage in Japan.

Materials research & development

USA

In the USA the Department of Energy (DOE) is funding research through its fossil fuel programme. This is wide ranging covering many materials addressed in this report with many of the same targets.

The DOE research on steam turbine materials for temperatures up to 760°C covers the development of Nibase alloys and coatings. Current programmes include:

- clean coal and natural gas (boilers, steam and gas turbines),
- carbon sequestration
- hydrogen and other clean fuels.

The programme is very active. The DOE portfolio also includes the challenging Futuregen programme. This is a 10 year \$1billion programme launched in 2003 that aims to build and run a ultra high efficiency (>60%) advanced coal based power station of approximately 275MW that will capture 90% of its carbon emissions and which will be the technology demonstrator for future power plant. The level and spend on these programmes is huge and increasing. Spend in 2008 on clean coal, natural gas carbon sequestration and hydrogen and other clean fuels is predicted to be \$426.6M, an increase of \$96M over 2007. Although not all this spend is on Materials it is indicative of the effort and importance attached to this subject in the USA.

In addition to this major integrated effort many US programmes are based on a single company using their own money and/or National funding and addressing their own specific needs, it is thus difficult to gauge the level of R&D that is currently active in these areas, especially given the complication of the aero derivative nature of many of the designs and Materials.



5.2 Future Specific UK Materials R&D Priorities

From the previous section a number of materials research programmes themes can be identified for each plant type. These are short to medium term (5-10 years) as they are identified solutions to current problems and are based on current technology. They involve incremental development of existing systems and technologies. These are:

- New, cost effective materials for boiler plant applications for operation at 700°C and above.
- Steam turbine materials for HP and IP operation at 760°C and above.
- Corrosion and fatigue resistant low pressure steam turbine materials for long term reliable operation up to 250°C.
- Cost effective, energy specific gas turbine materials for ultra high temperature operation.
- Advanced gasifier ceramics for reliable, long-term operation.
- Cost effective, corrosion and sulphidation resistant materials for gasifier gas coolers.
- Development of membrane-based options for separation of H₂/CO₂ for pre combustion CO₂ capture
- The effects of oxy-combustion on boiler environments and materials.
- Materials for bulk CO₂ transport.

As stated earlier these need to be undertaken in parallel with the underpinning coating, NDE, lifing, repair and joining technologies.

In addition to these there is a urgent need to launch and sustain the 'blue skies' research to identify the step change 'disruptive materials' technology that will provide a new generation of materials that enable ultra high efficiency operation. These will have a major impact on reducing emissions and are thus a key pat of the long-term solution. However, even with material and process modelling and understanding to reduce the costs and timescale, these will take 15-20 years to develop. This is thus a secondary priority to the programmes listed above but one that cannot be ignored, as it is the only solution for the long-term.

The above materials programmes are summarised for each plant type and in time order in the table opposite.

Component	Implementation timescale			
	5 years	10 years	20 years	
Boilers	 Production and characterisation of prototype components using advanced steels Understanding, characterisation and modelling of long term degradation of materials. Fireside corrosion studies on candidate tube materials for oxy-fuel technologies Development of surface treatments and coatings for protection against fireside corrosion and steam oxidation 	 Production and characterisation of prototype components using Ni-base alloys Development of multi- functional coatings for resistance to fuel contaminants 	 Step change disruptive materials technology for ultra high efficiency and low emissions. 	
Steam turbine	 Production and characterisation of prototype components using advanced steels Characterisation of improved material solutions for high temperature valve internals Characterisation of coating solutions for resistance to oxidation, solid particle erosion and water droplet erosion 	 Development of novel alloy/coating systems with both creep and oxidation resistance at temperatures >650 °C Development of welding consumables and long-term characterisation of high temperature welds Development of alloys with high strength, fracture toughness and SCC resistance for last stage LP blades 	 Improved understanding and predictive modelling of alloys and coatings for operation in plant with inlet temperatures >750°C Step change disruptive materials technology for ultra high efficiency and low emissions. 	
Gas turbine	 Development of existing materials classes to meet longer life/increase temperature requirements Coating technology to improve erosion/corrosion and temperature resistance. Repair and refurbishment technology for existing materials and plant. Advanced joining and bolting technologies Robust sealing technology 	 Development of integrated materials system solutions in existing and new classes of materials in all gas turbine components (eg. alloys designed for minimal degradation, materials systems for novel cycles) 	 Step change disruptive materials technology for ultra high efficiency and low emissions. 	
Gasifiers	 Improved corrosion resistance of refractories in gasification environments Qualification of refractories and coatings resistant to downtime corrosion Development of corrosion resistant coatings for syngas- fired turbines 	 Improved syngas cooler design and materials Improved gas cleaning materials (filters, sorbents and catalysts) Improved membranes for H₂ production from fossil and biomass/waste fuels 	 Materials for gasification system components in polygeneration for power, chemical feedstocks, hydrogen 	
CO ₂ capture	 Reliability of scrubbers downstream of existing system components Materials for the more aggressive fouling/ corrosion environment encountered in oxy-combustion Materials selection and corrosion studies for CO₂ pielines 	 Development of durable separation membranes Solvents and sorbents for CO₂ scrubbing Improved, high efficiency CO₂/H₂ membranes 	 Materials for advanced CO₂ capture concepts e.g. chemical looping Sensors for CO₂ pipelines 	
Generic To be done in parallel with all the above over all timescales	 Advanced manufacturing development for cost reduction, increased materials performance and integrity. Computer aided development and design of advanced materials and process modelling. Development and validation of improved life assessment procedures. Development of robust and accurate NDE methods. Facilities for extended exposure of materials to environments that reproduce service conditions. Research and development in joining technology. 			

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Key recommendations

- 1 The UK needs to develop an integrated structure for Energy Materials development that brings together the work being funded by industry, the research councils and other bodies so that the developments can be funded at an appropriate level, carried out in a holistic manner and can be delivered on the correct timescales. The infrastructure needs to span from the laboratory (academic) scale through to full-scale (industrial) validation and must include the inputs from other stakeholders, such as The Energy Technologies Institute.
- 2 The high level Materials R&D framework over 5, 10 and 20 years is:
- 5 years
- Incremental improvements in existing materials systems
- Production and characterisation of prototype components manufactured using identified materials and processes
- Repair and improvement solutions for existing plant and materials.
- Advanced manufacturing development for existing materials systems and processes aimed at cost reduction and increased performance and integrity
- 10 years
- Development of new material systems (substrate and coatings) based on existing knowledge including behaviour in realistic environments
- Development and application of process modelling to new materials to speed up introduction and help define new system solutions.
- Adopting a total system approach to critical part design and life prediction with multi-material components with joints and coatings.
- 20 years
- Identification of disruptive novel material systems and initial characterisation to identify most promising approaches
- Development of novel advanced technologies that will enable high overall efficiencies that will significantly reduce emissions.

- 3 In addition, there is an ongoing requirement for fundamental research in the following underpinning, generic areas without which recommendation 2 cannot be delivered:
- Surface protection technologies (Coatings).
- Improved understanding and predictive modelling of degradation mechanisms (Lifing).
- Non-invasive inspection techniques for in situ assessment of material condition (NDE).
- Existing plant refurbishment (Repair).
- Similar and dissimilar materials joints (Joining).

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- other members of the Materials community who contributed during the public consultation period of this report and the 2006 London Town Meeting.

CD contents

The CD appended to this report provides background information and materials technology priorities supporting the findings of this report. These include;

The individual reports on

- boilers,
- steam turbines,
- gas turbines
- gasification
- CO₂ capture

In addition, the CD includes copies of the full version of the Technology Status Review on Advanced Materials for Power Generation carried out as part of the DTI (now BERR) Cleaner Coal Technology Programme containing nearly 150 references. A shortened version of the same report is also included.

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