Advanced PF Power Plant – Improved Materials for Boilers and Steam Turbines

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Improved Materials for Advanced PF Boilers and Steam Turbines

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Project Partners :

Mitsui Babcock Energy Limited	(Co-ordinator)	(MBEL)
Alstom Power Ltd	(formerly ALSTOM Energy Limited)	(ALS)
Cambridge University		(CANTAB)
Corus UK Ltd	(formerly British Steel plc)	(COR)
Cranfield University		(CRAN)
E.ON UK	(formerly PowerGen plc)	(EON)
ESAB Group UK		(ESAB)
Loughborough University		(LU)
Metrode Products Limited		(MET)
National Physical Laboratory		(NPL)
RWE npower	(formerly Innogy)	(RWE)
Special Metals Wiggin	(formerly Inco Alloys Limited)	(SM)
Sandvik UK	(formerly Sterling Tubes Limited)	(SVK)
TWI		(TWI)

CONTENTS

DTI Cleaner Coal Project No. 132

Improved Materials for Advanced PF Boilers and Steam Turbines

1. BACKGROUND

In 1997 the Foresight Task Force identified advanced pulverised fuel technology as having the greatest market potential of the Clean Coal Technologies over the following 15 years. This task force, together with the Institute of Materials task force on materials, highlighted that the economic and environmental performance of this technology was currently limited by the performance of high temperature materials for boilers and steam turbines. As a consequence of this, the required R&D programmes perceived as being necessary for the development of improved materials were outlined.

The UK power generation industry responded to the recommendations partly through the present initiative, which is related to plant based on improved iron-based alloys. Although such plant will be able to operate at temperatures only up to 650ºC, the cost of the improved alloys will not be significantly higher than that of the alloys currently used, so that such plant will be competitive in terms of initial capital cost. The increased steam temperatures and pressures, which can be utilised as a consequence of new materials developed, will lead to significant improvements in plant efficiency, with consequent economic benefits and reduction in emissions.

The other avenue being separately pursued is that involving the use of nickel based alloys to allow even higher steam temperatures. This programme is receiving support through the EC's Thermie framework and from the DTI. It has a far longer timescale to fruition than the present initiative, as it will require inclusion of a demonstration phase. The technology involved in the present programme will be commercially exploitable much earlier, and, even after introduction of technology based on nickel based alloys, it will continue to be competitive in markets particularly sensitive to capital cost rather than through-life cost. The present programme is implemented through a wider European collaboration under the auspices of COST 522 (see below); as such collaboration reduces the costs of implementation and ensures that the UK remains abreast of the state-of-the-art in this technology.

2. THE COST FRAMEWORK OF PROGRAMMES

Over the last decade the Co-Operation in the field of Scientific and Technical research (COST) programmes have made a considerable contribution in improving power plant efficiency by advances in high temperature materials. The COST programmes are European wide, and operate under a management committee made up of representatives from the participating countries. A call for proposals is made across all these countries, and those received are reviewed for suitability on the basis of technical content and relevance to the overall COST objectives for that particular call. Upon approval, the successful organization is free to seek part or even full funding towards the work programme from government or other external agencies from their own country. In the case of the UK, this is the Department of Trade and Industry

(DTI), and careful selection and integration of programmes appropriate for the DTI's own Cleaner Coal Programme can enhance the value of the effort spent by including such programmes in the European COST initiative, as long as the aims of the two are compatible. As each participating country provides representatives for each project's steering committee, it also gives opportunities to ensure that the interests of the UK can be made known, progressed and safeguarded.

The stipulation within the membership of COST is that in any particular call, there will be free and full exchange of information, reports etc. developed during the programme period. In this way, with close collaboration both country-wide and Europe-wide, the costs of implementation of the R & D work are considerably reduced, or, of probably more importance, far more in-depth and wide ranging projects can be undertaken which would be well beyond the capabilities (or budget) of a single organization.

A number of the materials already developed in these programmes, e.g. in COST 501, the predecessor of the present programme, are in use in new plants across the world. Whilst significant benefits had been gained from the COST collaboration, it was however recognised that significant challenges still lie ahead. Accordingly, the major European power plant manufacturers proposed a new COST Project - COST 522: "Advanced Power Generation into the 21st century: Ultra efficient, low emission plant". This proposal was approved by the EU and obtained the signatures of endorsement by the participating countries government officials, including the UK, in 1998.

2.1 Aims and Objectives of COST 522

The objective of the COST 522 project was to develop and demonstrate the suitability of advanced components for the power industry. The operating temperature target for the steam plant was set at up to 650°C. With appropriate increases in steam pressure (>300 bar) and cycle optimisation, this will permit thermal efficiencies of 50% to be achieved. These targets are not based on developing an entirely new generation of ferritic, austenitic and nickel alloys but on the incremental development of the most advanced ferritic and austenitic materials currently available.

In addition the action took the strategic view that alternative cycles and fuels will play a major part in future world power generation. Although much of this may be beyond the five year timescale of this project, it was recognised that significant work needed to be performed on gasification technologies, high temperature heat exchangers, hot gas clean up etc. For this reason some of this development work was performed within COST 522 with a view to securing the long-term future of the power plant industry.

2.2 Organisation of COST 522

The overall COST 522 project was divided into three main working groups related to individual critical components, viz. Steam Power Plant, Gas Turbines, and Plant Integration and Ancillary Components. In addition, Common Activity Groups were set up related to technologies important to all these components, viz. Welding, Metallography and Alloy Design, Oxidation and Protective Systems, and Modelling. Over one hundred organisations from seventeen European countries participated, including twenty-two organisations from the UK. Fifteen of these organisations collaborated to produce a proposal, Project No. 132 in the DTI Cleaner Coal Programme, covering items of UK interest in the Steam Power Plant and Plant Integration groups. The former (Steam Power Plant) was further divided into Boiler and Steam Turbine aspects, and these groups, their objectives, the UK participants and the project deliverables are listed below. A full list of participants is also given on the first page of this report, and contact details in the Appendix. Some companies have changed their names during the course of the project, and for consistency throughout this report, the present names of the companies participating are used. These companies are: Alstom Power Ltd (formerly ALSTOM Energy Limited), Corus UK Ltd (British Steel plc), E.ON UK (Powergen plc), RWE npower (Innogy), Special Metals Wiggin (INCO Alloys Limited) and Sandvik UK (Sterling Tubes Limited).

Boiler Group

Participants	Objective	Project Deliverables
Pipe and Tube ***Cambridge U*** *Corus* *E.ON* *RWE npower* *Loughborough U** *Metrode** *Mitsui Babcock* *Sandvik UK*	Development of improved alloys for superheaters, headers and pipework and prototype component manufacture and characterization.	• Production and assessment of UK advanced ferritic steel based on DTI funded PIPPE work • Production and assessment of advanced austenitic steel based on E1250 • Development and assessment of welding consumables
Furnace walls *Mitsui Babcock*	Development of improved alloys for furnace walls. Prototype component manufacture and characterization.	• Design and test suitable weld consumables • Assess potential failure mechanisms
Fireside Corrosion *Mitsui Babcock*	Identification and testing of viable coating materials.	• To identify viable coating materials for superheater tubes and furnace walls in coal fired plant

* Loughborough University and Metrode programmes applicable to both Boiler and Welding Groups

Steam Turbine Group

Forgings *Alstom*	Development of improved alloys for high temperature rotor forgings and prototype component manufacture and characterization.	• Improved alloys for high temperature forgings
Castings *Alstom* *E.ON*	Development of improved alloys for high temperature castings. Prototype component manufacture and characterization.	• Improved alloys for high temperature castings • Materials data for plant life assessment under flexible operating regimes
Bolts *Alstom* *Corus*	Development of improved alloys for high temperature bolting.	• Development of nickel-based alloys optimised for bolting of 9-12%Cr ferritic steels • Development of high strength ferritic bolting steel

Common Activity Groups

Welding *TWI* *ESAB* *Loughborough U** *Metrode**	Development and modelling of welding procedures and consumables required for the different Component Groups.	• Production and assessment of consumables for advanced ferritic steels • Assessment of welded joint mechanical properties • Investigation of metallurgical mechanisms involved in developing strength, creep resistance and toughness in these materials
Metallography *Alstom* *RWE npower* *Cambridge U*	Accelerated alloy development and application through improved understanding and modelling of microstructural evolution and its relation to mechanical properties.	• Quantitative descriptions of microstructural evolution • Models for microstructural evolution • Models for creep behaviour

* Loughborough University and Metrode programmes applicable to both Boiler and Welding Groups

Oxidation *Alstom* *NPL*	Characterisation of steam oxidation behaviour of new alloys. Development of surface engineering technologies to provide enhanced oxidation resistance where required.	• Steam oxidation rates for new 9-12%Cr steels • Surface engineering technologies for improved oxidation resistance • Development of validated oxide scale spallation map for 9-Cr steel, supported by appropriate data

Plant Integration Group

Corrosion and Life Prediction *E.ON* *Cranfield U*	To produce corrosion design maps and life prediction models for coal and co-fired combustion plant.	• Database of laboratory and plant data (corrosion data, fuels/operating conditions) • Component life prediction models • Assessment of monitoring systems

3. TECHNICAL AND ECONOMIC VALUE

By the implementation of DTI Project 132 and participation in COST 522, the UK gains improved potential for export and thus overseas earnings through the materials suppliers gaining new markets for their products, the plant manufacturers gaining a competitive advantage over their rivals and utilities offering improved economic and environmental performance. Domestically, UK utilities will have access to technology offering improved economic and environmental performance, offering benefit to UK society and industry in general.

The COST 522 project with its objective "to develop and demonstrate the suitability of advanced components to permit thermal efficiencies of 50% for power plant" is in harmony with the UK Foresight targets, by:

- enabling the UK power generation industry to develop its technological capability to secure a significant share of the world market
- acting as a focus for collaboration between industry, universities and European organisations
- enabling the DTI to contribute to the decrease in CO_2/MW as efficiency increases.

4. BOILER GROUP ACTIVITIES

UK organizations have been involved in the development of ferritic/martensitic alloys for superheaters, headers and pipework, austenitic alloys again for superheaters and reheaters, and welding consumables for these applications. In addition weld consumables for furnace wall alloys have been developed and tested. Metallic coatings suitable for corrosion protection in superheaters and furnace walls have also been investigated.

4.1 Low Alloy Ferritic Materials

Starting at the low end of alloying content, there is significant interest in the newer 2¼%Cr steels for furnace wall fabrication. Advanced boiler designs at Mitsui Babcock have higher efficiencies, which derive from the thermodynamic advantage of operating at higher temperatures than at present. Unfortunately, the higher temperature furnace wall temperatures involved have revealed a material constraint. The required better oxidation resistance and improved long term strength necessitate the use of a more highly alloyed steel and this in turn would normally lead to a requirement for post-weld heat treatment (PWHT) on the welded panels to reduce the hardness to an acceptable level. Because the materials in the panel are relatively thin and extended surfaces are involved, considerable distortion can occur during PWHT, leading to major problems of fit-up during erection and extra residual stress deriving from remedial adjustment. It is therefore highly desirable to avoid PWHT, which, if it is unavoidable, also carries a commercial penalty.

4.1.1 Membrane Panel Manufacture

Two steels have been developed which are suitable candidates for this particular role: the relatively inexpensive, low alloy HCM2S (generic name T23/P23) and the more expensive, high alloy HCM12. Examination of the "Allowable Design Stress vs. Temperature" curves of these two steels indicates that below about 550°C there is no advantage of HCM12, while above that temperature, although the HCM12 is superior, the strength of both steels falls off very rapidly with increase in temperature. For economic reasons it was therefore considered useful to examine the possibility of using HCM2S in furnace membrane panels.

Initially it was necessary to demonstrate that the fabrication procedures used to manufacture the boiler components could in fact be performed satisfactorily on the materials involved, and the first task was to manufacture a demonstration membrane panel. The welding was carried out on a commercial submerged arc panel-welding machine (Walther Panel Welding Machine, shown in Figure 1) which produces two fillet welds simultaneously on either side of the tube. Initial tests were carried out both with and without preheat to ascertain the effect this would have on the hardness of, in particular, the T23 tube heat affected zone.

The values obtained are shown in Table 1, and were effectively the same with or without preheat. They also indicated that post weld heat treatment was not necessary, the hardness values being well below the maximum permitted by BS 1113 for avoidance of PWHT. Accordingly, the full scale mock up, consisting of an 8 tube wide by 3 metres long assembly, was welded without either preheat or PWHT. The membrane strip used was standard 1Cr½Mo and the welding procedure and consumables were otherwise as used for conventional low alloy (1 Cr to 2¼Cr) fabrications. The resultant fabrication was successfully bent through 90° to a radius of 300mm, being typical for this size of tube, in a brake press (Figure 2). The entire operation was considered to have been very successful; the finished article is shown in Figure 3.

4.1.2 Weld Consumable Development - Mitsui Babcock

The commercially available HCM2S manual metal arc electrodes, when tested in the as welded condition, had been found to markedly over-match the parent material requirements. Several formulations of electrode with varying levels of carbon and tungsten were therefore produced and various tests including hardness and tensile tests conducted on the resultant weld pads. These data were used to develop the neural network programme produced by Cambridge University, which provided the final chemistry limits for a new electrode designated Babcock J type. This was considered to provide appropriate mechanical properties in the as welded condition. However it was subsequently shown that when post weld heat-treated, under matching creep rupture life was obtained and consequently for stress relieved weldments it was decided to revert to a more matching chemistry. This was done, again with the aid of the neural network package at Cambridge University, and a new electrode produced which, on the basis of some limited testing, provided creep properties, which were deemed acceptable. The preliminary and final batch results are given in Table 2. Limited cross weld stress rupture results at 550ºC are shown in Figure 4.

Weld Procedure Qualification tests were then conducted on various dissimilar weld combinations with T23, and also on a thick section weld, which was given PWHT. All were found to be satisfactory.

A final exercise was conducted to determine the susceptibility of the material to reheat cracking. It was decided that this would be undertaken using bulk quenched samples of HCM2S material, heat treated in a manner to produce grain sizes similar to the measured coarse grained heat affected zone from typical weldments.

It was found by experiment that a warm water quench from 1060°C of 30mm thick blocks of the material produced the required grain size. Elevated tensile tests were then carried out over a range of temperatures using a low strain rate and the resultant elongation and reduction of area (R of A) measured on each sample. The results of two tests are given in Figure 5. Although a reduction in ductility was observed between 650°C and 750°C, the measured reduction in area was in excess of 20%. It was therefore concluded that the material exhibited a low susceptibility to reheat or stress relief cracking.

Overall, the project was successful in:

- Satisfactorily fabricating a membrane panel assembly including ninety degree bend
- Developing satisfactory procedure qualification tests with T23
- Developing manual metal arc consumables for T23
- Demonstrating acceptable stress rupture values for weldments in T23
- Demonstrating low susceptibility for T23 to exhibit reheat cracking

The programme has demonstrated that T23 in thin section will be a suitable alloy for furnace wall fabrication, and also, due to its lack of PWHT requirement, for repair of such fabrications should it prove necessary in later component life.

4.1.3 Weld Consumable Development - Metrode

Metrode's participation in the Boiler Group is concerned with developing welding consumables for the new advanced creep resisting materials. The first stage of the project involved Cr-Mo ferritic steels, which included T23, as well as the higher Cr grades, which are covered later. A particular focus has been concerned with consumables for Flux Cored Arc Welding (FCAW).

Table 3 gives representative all-weld metal compositions for the three variants of Shielded Metal Arc Welding (SMAW, or Manual Metal Arc, MMA) electrodes and two variants of FCAW electrodes for which mechanical properties are tabled in the following sections. One of the electrodes (Chromet 23L) has a low carbon level around 0.05% and a deliberate nickel addition, aimed to optimise as-welded toughness. A batch with low carbon but without Ni addition was also tested for comparison. The other (Chromet 23H, not currently a production variant) is closer to base material composition, with no nickel and a little more carbon, possibly more appropriate where heat treatment will be applied. In the course of development many other experimental batches of SMAW electrodes with minor variations were tested and the results are used to illustrate some relevant trends. In the same table, two variants of weld composition of flux-cored wire are also listed; one has nickel addition while the other has slightly lower C and Nb contents without Ni.

The development work was carried out in such an order that the alloying/flux designs were checked against their welding operability, the best candidates then being subjected to further mechanical tests. All-weld metal test coupons for mechanical properties were prepared in general accordance with AWS-ASME procedures using low carbon steel plates of thickness 13 or 19mm (25mm for CTOD tests) as appropriate to the welding process or electrode size, with 10-degree bevelled edges buttered with two layers of the test weld metal. Each strongbacked assembly with backing strip was held at a preheat-interpass range of 150-200°C for T23 consumables. The groove was filled using two beads per layer in most cases, while some welds were specially prepared for investigating the effect of bead arrangement. When PWHT was applied, test coupons were furnace cooled. Tests included ambient and elevated temperature tensile, hardness, and Charpy impact tests.

Table 4 gives some representative all-weld metal tensile test results. In all cases the weld metals were sufficiently strong, and the very high strength without PWHT reflects as-welded hardness values of 290-350HV, which fell below 250HV after PWHT at 715°C for 2 hours. Hot tensile tests up to 550°C were also conducted on FCAW weld metals. The strength of FCAW weld metals exceeded parent material minimum at all temperatures. At temperatures beyond 450°C, the 0.2% proof strength of the earlier version of FCAW (Cormet 23-A) started falling below the typical levels of T23 tubes/pipes and was rapidly approaching the base material minimum. As expected, the modified version (Cormet 23-B) with higher C and Nb considerably improved strength, particular at higher temperatures (450-550°C), and comfortably matched the typical 0.2% proof strength.

During SMAW development work, a slice from every all-weld test piece was surveyed for hardness at cap and mid-section. The grossed average as-welded hardness of cap and mid-section (25 batches) was 329HV, and although some of the highest individual values were found in the cap, about 60% of tests were slightly harder in mid-section. A hardness below 350HV was considered desirable but a number of tests exceeded this. However, these numbers conceal underlying trends related to changing composition, and the weld cap or mid-section hardness generally increased as a function of a 'carbon equivalent' parameter. Most of the harder welds, irrespective of carbon level, were those with Ni added, or those without Ni but with higher carbon.

Results of the all-weld metal Charpy impact tests at 0°C and 20°C for representative batches of SMAW and two batches of FCAW are given in Table 5. In the cases of SMAW, most testing was carried out on the Ni-bearing SMAW welds without PWHT. The Ni-free SMAW and FCAW welds were satisfactory at 20°C after PWHT at 715°C. At 0°C, however, FCAW was distinctly lower in toughness after 2-3 hours PWHT than SMAW after only 30 minutes, whereas the FCAW variant with added Ni and higher C, Nb and B showed a significant improvement. The as-welded toughness of the Ni-free SMAW and FCAW welds was considered borderline at room temperature and unsatisfactory at 0°C.

4.2 Higher Alloy Ferritic/Martensitic Materials

One family of steels that has received considerable attention is the 9-12%Cr martensitic types. These offer greater flexibility of operation for thick section boiler components over more creep/oxidation resistant austenitic steels due to their lower coefficients of thermal expansion and better thermal conductivity. They are also cost effective as a result of the lower alloy content, particularly of expensive additions such as nickel.

4.2.1 Alloy Development

Recent developments have included grades such as Steel 92 (P92, T92) containing 9%Cr which gives a 100MPa/10^5 hours rupture life at temperatures approaching 620°C, the highest among commercially available ferritic grades. However to achieve enhanced steam oxidation resistance chromium contents above 9% are required. This project in the COST 522 collaborative programme, conducted by Corus, has sought to establish a martensitic 11-12%Cr base composition with better creep strength and oxidation resistance than P/T 92.

The following factors were considered to be applied to an 11% Cr base:

- Avoid suppression of the α/γ transition temperature to permit the use of the maximum tempering temperature [1].
- Obtain microstructural stability through use of low levels of residual elements to reduce coarsening rates of precipitates [2,3].
- Use Mo and W to provide rupture strength by solid solution strengthening and Laves phase precipitation.
- Use high W to Mo ratio to optimise the long-term stability of Laves phase precipitates [4].

This led to the design of three development alloys. The first alloy contained lower residual levels (Si, Mn, Ni, Al) than found in conventional 9-12%Cr grades. The level of Mo was set at1%, W at 0.30% and Co at 2.0% the latter to help suppress delta ferrite. The second alloy is of the same base composition but with Si, Mn, Ni and Al levels more typical of those which can be readily achieved in large scale electric arc steel making. The third variant contained higher W (2.0%) and lower Mo (0.50%) levels than the other two. A 50kg air induction melt was produced for each of the development alloys, and their chemical analyses are shown in Table 6.

The tendency to form delta ferrite on heating was determined metallographically from 40mm long bar samples held at selected test temperatures between 1200-1350°C for 30 minutes, followed by water quenching. Except at 1350°C, which is well above reheating temperatures for hot working, where delta ferrite was observed, the levels in the experimental alloys were below those found in Steel 92 for any given temperature.

Phase transformation temperatures were determined by dilatometry, and shown in Table 7, and Table 8 gives the room temperature mechanical properties. Some data from currently used 9-12%Cr steels are also given in these tables for comparison.

Stress rupture tests have been initiated with target lives up to 30,000 hours, with the longer-term tests continuing beyond the end of this programme. The results of the initial testwork are given in Figures 6 – 8, where it can be seen that of the experimental alloys, the high tungsten low molybdenum alloy so far is showing the best performance. Tungsten and molybdenum improve rupture strength both by solid solution strengthening and by the precipitation of Laves phase, $Fe_2(Mo,W)$. The long-term stability at temperature of Laves phase is enhanced at higher concentrations of tungsten [4]. The rupture data for the Mo/W alloy, and Steel 92 data have been fitted using a Larsen-Miller Parameter (LMP), Figure 9. Both data sets fitted well for a C value of 30, and based on the short-term data the Mo/W alloy produces similar rupture performance to T 92 at temperatures up to about 615ºC for lives up to about 10^5 hours. However, the steeper gradient of the Mo/W line gives reason to be cautious about the long-term rupture properties. The data in the present paper and from other sources indicate that the use of cobalt in conjunction with molybdenum and tungsten leads to reduced long-term microstructural stability. This is almost certainly due to the influence of cobalt in reducing the solubility of molybdenum and tungsten, thus accelerating precipitation kinetics of Laves phase. The long-term stability of these 12%Cr steels is also limited by the formation of Z-phase, (Nb,Cr)N.

Although the rupture properties of the development alloy are only similar to those of T92 and not superior, the steam oxidation resistance shows a very significant improvement. Steam oxidation tests were carried out on samples from the development alloys together with a sample of commercial P92 in the same furnace, and tested at 650°C for times up to 5,000 hours. Samples were removed from the furnace and the weight change measured at several points during the test. Results are shown in Figure 10, where the development alloys with chromium levels of 11% all showed a noticeably greater oxidation resistance than commercial P92 with 9%Cr. After around 5000 hours, weight gains for the development alloys were 0.17mgcm^{-2} (normal residual), 0.20mgcm^{-2} (Mo/W) and 0.62 mgcm^{-2} (low residual), which compared to 25.8mgcm^{-2} for P92.

4.2.2 Welding Development

As well as the work on T23 weld consumables summarised earlier, Metrode also performed similar assessments on advanced consumables for P/T92 material, E911 and P122.

P92 Testwork

All-weld metal tests were conducted and Table 9 gives the typical compositions of different welding processes with parent material specification for comparison. These compositions are similar to the parent material except that more Mn is allowed and some Ni is added . As with weld metals for P91, Ni helps to ensure optimum toughness.

All-weld metal tensile tests were carried out for GTAW, SMAW and FCAW processes at room and elevated temperatures after PWHT at 760°C. Table 10 gives the representative results, with typical hardness values. Room temperature strength after 2-4 hours PWHT comfortably exceeded P92 base material requirements, and except for GTAW having a small ductility advantage, there were no remarkable differences between processes. Plots of proof and tensile stress results, e.g. Figure 11, show that all three processes are similar, with some convergence to base material minimum towards 650-700°C.

Hot tensile test specimens had a gauge diameter of 5.0mm and there was some evidence that strength values may be conservative when compared to results from specimens with larger gauge diameter (for example 10mm, not reported here). The hot tensile strength was comparable to P91 weld metals previously reported elsewhere. Interestingly, comparisons of published minimum and typical hot tensile properties for P91 and P92 parent materials also show relatively little difference between the two alloys, despite the significantly greater creep rupture strength of P92.

Representative impact toughness results are given in Table 11 for all welding processes. There was a noticeable benefit of increasing PWHT from 2 to 4 hours at 760°C, and there were also differences between welding processes. As expected, GTAW weld metal was the toughest owing to its low oxygen (hence low non-metallic inclusion) content compared to the flux-related SMAW, FCAW and SAW processes. A contributing factor to the lower FCAW toughness is believed to be residual Ti arising from rutile, which is an essential component of the flux system for all-positional operability. PWHT duration of 4h is therefore considered most prudent for FCAW welds. Toughness may be a particular concern with respect to hydrotesting upon the completion of major fabrication.

Relationships found between impact energy and lateral expansion are shown in Figure 12. This plot includes additional statistics from development data, as well as tests at 0°C and 20°C. When compared to the average trend previously established for P91 weld metal, at the same absorbed energy the notch ductility of P92 welds appeared a little higher.

It has been reported by some researchers that welding position, weld pass sequence and the bead thickness had a considerable effect on impact toughness of P91 weld metals, so an investigation was carried out to explore such possible effects with the FCAW process for P92. Four AWS-type butt welds were prepared: two welded at ASME 1G and two at 3G positions. At each position, one weld was deposited using two split beads per layer while another used full width weaved single layer beads. After PWHT of 760°Cx4h, the weld metals were subjected to Charpy impact testing at 20°C, however the results were rather inconclusive. This broadly agrees with results reported by the authors in an earlier research concerning P91 SMAW weld metals.

P122, E911 Testwork

The earlier development of an E911 SMAW electrode had been completed by Metrode within the previous COST 501 project and the product is commercially available for fabrication. Preliminary development work has been carried out for the equivalent flux cored wires for E911 and P122. Table 12 shows the typical undiluted all-weld deposit compositions and Table 13 lists the impact toughness and hardness of the weld metals. The results indicate that E911 flux cored wire of the current design delivered an identical toughness to the FCAW weld of P91 alloy and is considered acceptable. The FCAW weld metal for P122 alloy, on the other hand, showed poor properties and further work is required. This will be considered should the prospective of the future application of P122 base alloy become clearer.

Fracture Toughness Assessment of FCAW Weldments

Fracture toughness CTOD tests were conducted according to BS7448 on 20mm BxB specimens notched from the weld top. These were extracted from a 25mm thick test coupon welded according to AWS procedures with P91 FCAW. The PWHT chosen was 760°C×2h+FC, which gave average Charpy energy values around only 20J. When specified, code criteria are above this level.

Based on a minimum specified water inlet temperature of 7°C for hydrotesting, CTOD tests were carried out at two temperatures, namely 20°C and 0°C. The results indicated values for the FCAW weld metal in the range of 0.018mm to 0.030mm, with small (but probably insignificant) variation between the values at 20°C and 0°C.

The lowest of 6 measured individual CTOD values (δC = 0.018mm at 20°C) was used in calculating a maximum tolerable flaw size, using TWI's Crackwise® software which automates engineering critical assessment procedures set out in BS7910. The model chosen was a fabricated header of 450mm outside diameter and 50mm wall thickness and design conditions were taken to be 176 bar at 580°C, with hydrotest conditions of 1.25 times design pressure at ambient temperature. The results indicate a maximum tolerable surface flaw size of 125mm in length and 12.5mm in depth for a longitudinal seam weld, i.e. equal to ¼ of the wall thickness. When plotted on a failure assessment diagram, the results indicate a good defect tolerance despite the relatively low fracture toughness, so Charpy values around 20J can be considered fit for purpose.

4.2.3 Effect of Alloying Elements on Microstructure of 9-12%Cr Weldments

The effect of alloying, in particular the balance between ferrite- and austenite/martensite-promoting on microstructure and toughness has been studied by Metrode. A group of SMAW electrodes was produced to provide a matrix of systematically varied compositions. Table 14 lists the 16 weld metal compositions. These are divided into four groups, each with at least one different element in the base composition, which was held constant, while chromium was progressively increased in four steps (the average percent is given for 'non-varying' elements in each group, since the in-group variations of these were small). Before testing, the weld blocks were subjected to a PWHT at 760C for 2 hours followed by a furnace cool. A vertical slice from each block was metallographically assessed by University of Loughborough for delta ferrite content, using point-counting method. The results were then assessed against previously established constitutional factors such as those given in Table 15 that predict the tendency of particular compositions to form delta ferrite.

Results indicate that the coefficients proposed by Ryu and Yu (Figure 13) incorporate the effects of the alloying elements involved in the current investigation better than the relationships proposed by many earlier researchers. Based on the Ryu & Yu relationship, it is suggested that to minimise the ferrite content, Creq of a 9-12%Cr ferritic weld metal composition should not exceed 9-9.5%.

Charpy impact tests were conducted at ambient temperature on weld metal sampled from the undiluted upper section of the weld blocks. The results are plotted in Figure 14 against the corresponding assessment of delta ferrite for each variant. From the trend it is apparent that for a Charpy energy >30J at 20°C, a microstructure with <0.5% ferrite is desirable. For a Charpy energy above 30J, the Creq based on Ryu and Yu coefficients should be controlled to a level of <9.5-9%, (Figure 15) which coincides with the level required for minimising delta ferrite in the microstructure to<0.5%.

The toughness of FCAW weld metals of P91, E911 and P92 are plotted against Cr eq from Ryu and Yu (Figure 16). Interestingly, a Creq of <9% is also found desirable for achieving an acceptable level of toughness (e.g. >20J at 20°C).

4.2.4 Implications of Weld Metal Creep Ductility for Plant Integrity

The aim of this programme was to investigate the potential implications of low weld metal creep ductility for plant integrity, and hence develop better consumables for advanced plant. The main part of this programme was carried out by E.ON (formerly Powergen) with contributions from Metrode Products Ltd and Mitsui Babcock.

Part of the testwork was aimed at clarifying how creep damage development is related to the creep curve. The project was designed to compare parent P91 with a conventional manual metal-arc weld metal, Metrode Chromet 9-B9, and a recently developed flux cored arc weld metal, Metrode Supercore F91. Alternative post weld heat treatment and ageing conditions were also explored. Weld pads were supplied as-welded by Metrode for PWHT and ageing at Power Technology.

Chemical analysis and hardness data are given in Tables 16 and 17. No significant differences were found between columnar and reheated weld metal hardness.

The Supercore F91 rutile FCAW deposit is metallurgically quite different from a conventional MMA consumable, with substantial titanium pick-up from the flux, counterbalanced by a much reduced niobium content. This increases temper resistance [5]. The HT1L, HT2, and pre-aged conditions produced average hardness levels of 284, 244 and 227 VPN respectively, demonstrating that this weld metal is intrinsically much stronger at ambient temperature than MMA alternatives.

Short term creep testing to failure was designed to achieve test timescales of the order of 1000 hours, so that substantial data could be generated for a variety of stress and temperature conditions within a reasonably short time. Creep tests were carried out within the following ranges of conditions:

- A realistic service temperature but very high stress: 600°C / 120-190 MPa
- Accelerated temperature and accelerated stress: 650°C / 80-130 MPa
- Very high temperature but a realistic service stress: 690°C / 50-80 MPa

Thus, the test stress was designed to vary from a high fraction of flow stress (tests at 600°C) to a moderately low fraction of flow stress (tests at 690°C).

All-weld metal specimens were tested with specimen axes longitudinal (aligned with the welding direction). Crosshead creep strain was monitored throughout each test. A linear best fit to the data was then used to identify the approximate beginning and end of the secondary creep regime, during which the strain rate is approximately constant.

Figure 17 shows the creep rupture data. Parent data are shown black, MMA blue, and FCAW red: open symbols and dashed trend lines denote pre-aged materials: and larger, bolder symbols indicate increasing test temperatures. The data were analysed in many different ways, as indicated below:

- Life vs. creep strength (applied stress relative to the BS PD 6525 value for parent corresponding to the failure time achieved)

- Mean secondary creep rate vs. applied stress
- The Monkman-Grant ductility parameter (defined as the product of mean secondary creep rate and time to failure) vs. applied stress
- The Monkman-Grant values at constant creep life instead of constant stress

The shapes of the creep curves were also analysed in more detail to assess the factors affecting deformation and ductility. It can be argued that, if the critical concern is that weld metals reach the end of secondary creep at lower strains than parent materials (and then begin rapidly to accrue damage, whether in the form of creep cavitation or microstructural degradation), then the important parameter to assess is the total strain accrued up to the end of secondary creep. However, this "secondary plus primary ductility" parameter shows a rather confusing, scattered dependence on the test variables. It proved to be more profitable to analyse separately the "primary ductility", i.e. strain accrued to end of primary creep, and the "secondary ductility", and i.e. strain accrued within secondary creep. This shows that quite different factors govern these different stages of the creep curve.

Tentatively it was concluded that the Monkman-Grant parameter was the best practical measure of the relative secondary creep ductility's of weld metals and parent material. However, a more rigorous analysis of the shapes of creep curves will be needed to clarify tertiary creep behaviour.

For interrupted creep tests, a suitable test stress for each material and temperature was selected. A series of crosshead strain monitored interrupted tests was then carried out, to different interruption strain levels, at the selected test stress. The interrupted test specimens were measured to determine elongation and diametral reduction data, sectioned longitudinally to determine corresponding hardness variations along the gauge length, and examined after careful etch polishing to determine the extent of any optically detectable creep damage.

Parent material tests were interrupted at a series of strain levels, but damage was only generally detectable around 7-8% strain, typically corresponding to over 90% life fraction. The inescapable conclusion is that failure of P91 parent material is principally caused by strain - induced microstructural degradation and hence accelerated creep deformation into the tertiary regime.

A similar exercise was then carried out on weld metal specimens, and the results were qualitatively quite different. While some weld metal specimens interrupted just inside the tertiary regime did still appear to be undamaged, those that had accrued any substantial tertiary creep strain generally showed substantial microcracking or macrocracking damage.

It is not clear whether creep damage is itself the main cause of the secondary to tertiary transition observed in weld metal creep tests. There appears to be a broad correlation between the onset of damage and the onset of tertiary. However, the level of damage observed appears to be too minor to cause the observed strain rate increase simply by its effect in reducing the specimen net section. It may be that creep damage also affects the creep rate by other mechanisms, and/or, that creep strain accumulation causes a continuous progression from microstructural degradation (change in particle/matrix interface structure from coherent to incoherent) to actual creep damage (decohesion at the particle/matrix interface leading to cavitation and/or cracking).

The work has indicated that low weld metal secondary creep ductility is a significant concern in high alloy steel. Generally, it appears to be a lesser threat to long-term plant integrity than HAZ Type IV cracking, but the risk of eventual transverse weld metal cracking in pipe and header butt welds should not be ignored.

For the above programme, weld metals in the form of as-welded pads were provided to E.ON by Metrode. A small number of tests were also performed by Mitsui Babcock on weld metal specimens produced using their own M type electrode. A number of test plates were welded and stress relieved at 765ºC to provide all weld creep specimens. It was decided that interrupted tests would be conducted at 650ºC and 100 MPa, giving an approximate expected failure time of around 1500 hours. On the first few tests a large amount of scatter in failure times was experienced, such that some tests, which were to be interrupted, failed before the required duration was reached. In an effort to discover the cause, e.g. possibly poor properties in one of the test plates, a total of 11 tests were conducted, and these gave a scatter in failure lives of 91 to 1655 hours. The specimens with the short duration lives showed far greater elongation than the longer term ones.

The excessive scatter did not appear to correlate with a particular test plate, so properties measurements and detailed metallography were performed on a number of specimens. It was concluded from these that the problem concerned the variable microstructure seen in the specimens. For the low strain specimens there appeared to be a local prevalence close to the fracture face of as deposited metal with columnar grains whose boundaries were aligned approximately parallel with the fracture plane. In these specimens the creep damage was predominantly, but not exclusively at these boundaries, present as creep microcracks, with little reduction in area at the fracture face. In the high strain specimens there appeared to be less evidence of columnar grain boundaries oriented parallel to the fracture face. The creep damage was more evenly distributed as cavitation on grain boundaries and carbides.

It was considered that the incidence of columnar grain boundaries perpendicular to the stressing direction was possibly due to sampling during manufacture of the (relatively) small specimens (9 mm diameter, giving a cross section of 64 mm^2). Two further tests were therefore initiated using 100 mm^2 cross-section stress rupture specimens cut from one of the same plates previously used. Failure times for these were 721 and 868 hours, i.e. relatively close to each other and near the centre of the previous scatter band. When plotted on the same graphs as the E.ON results above, the latter cut across the scatter band in the Mitsui Babcock specimens at a reasonably central position, and close to the failure durations of the larger diameter specimens.

4.3 Austenitic Materials

The major effort in this part of the programme has been provided by Corus, with a smaller section of the testing being undertaken by Mitsui Babcock.

Esshete 1250 (15%Cr 10%Ni 6%Mn 1% MoVNbB) is an austenitic stainless steel that has been used successfully as a superheater/reheater boiler tube material currently operating at temperatures of 600-620°C, mainly in UK power stations. However, for further improvements in the efficiency of pulverised fuel (PF) power plant, tubing materials will require increased strength and oxidation/fireside corrosion resistance in order to operate satisfactorily at higher service temperatures.

There are other austenitic grades currently available with properties claimed to be suitable for use under more demanding service conditions. These are Japanese developments, primarily NF709 (21%Cr 25%Ni 1.25%Mn 1.50%MoNbB), which is considered by COST 522 as the benchmark, but suffers from a high cost. Esshete 1250 has also been used as the inner material of a co-extruded tube, but again such a composite material is very expensive. Thus, there is a need to develop a European grade with similar properties to NF709, which is less costly.

The main aim of this work package was to develop from the basic composition of E1250 an advanced austenitic alloy grade with improved oxidation and corrosion resistance, and creep properties, suitable for service temperatures of 670°C without the need for a manufacturing route involving co-extrusion. It is essential that other features of E1250, adequate formability for tube/pipe/header manufacture, microstructural stability, good weldability and low delta ferrite content are retained.

During the early part of the work programme a number of activities were undertaken by Corus and the COST 522 boiler group as part of a conceptual study. On the basis of this study four development compositions were established by Corus. The Cr level was set at 23% for better steam oxidation and hot corrosion resistance. Levels of 6-9%Mn, 15%Ni and 0.1-0.2%N were utilised for austenite stability. Additions of Cu and W were made for improved creep strength. Nb levels were reduced from 1.0% to 0.2-0.6%. For each of the alloys a vacuum induction melted experimental 50kg ingot was produced and subsequently processed by forging and hot rolling to 20mm diameter bar, and cast analyses are given in Table 18.

Microstructural characterisation studies comprised optical metallography, hardness testing, delta ferrite assessment and electron metallography. In comparison to commercial NF709, the closest grain size and hardness values for BGA1, 3 and 4 were found to be at the highest solution treatment temperature of 1200°C and so this was utilised for specimens for stress rupture testing.

Mechanical Testing

Room temperature tensile and impact data for 1100°C solution treated material are given in Table 19 along with typical values for E1250 and NF709 products [6]. Values in brackets for BGA3 and BGA4 are for 1200°C solution treated material.

Proof strength and tensile strength values for BGA2, 3 and 4 solution treated at 1100°C were higher than those of typical values for E1250 and NF709 although more so for the former. Elongation values were slightly lower. Charpy impact values for BGA3 and 4 were above 100J. The mean value for BGA2 was below 71J but was not considered to be especially low. For BGA1 the proof strength and tensile strength properties are above E1250 typical values but below those of NF709.

Higher solution treatment temperatures for alloys BGA3 and 4 caused a reduction in both proof strength and tensile strength, with a corresponding increase in ductility, and greater impact resistance.

Stress Rupture Testing

Stress rupture tests were carried out at 650°C and 700°C (Corus) and 675ºC (Mitsui Babcock) using stress levels designed to give aim lives of 1000h, 3000h, 10,000h, 30,000h and 100,000h. The stresses were based on data for NF709.

For the low Nb alloy a single test at 650°C/240MPa gave a life of 816 hours. This was below the predicted life of 1000 hours and those of the other three alloys, which gave lives of between 1296 to 3129 hours at the same stress level. It was therefore decided at an early stage of the stress rupture test programme not to continue with the testing of the low Nb alloy.

Results so far on the other alloys are shown in Figures 18-20. The stress rupture test programme at 650°C, 675°C and 700°C has some of the longer-term tests still in progress. Out of the four compositions studied the alloy with a 23%Cr/15%Ni base composition containing additions of 1.4% tungsten and 3% copper, BGA4, exhibited the best creep strength. The alloy with a higher Mn content of 10%, BGA2, gave a disappointing performance at all three test temperatures. Rupture lives for the alloy with a 3% copper addition made to the base composition, BGA3, were intermediate between those of BGA2 and BGA4.

Rupture lives to date for completed tests on the base+Cu+W alloy, BGA4, out to 10,000 hours show a performance comparable to that of NF709 up to 675°C. Data for BGA4 are compared using a Larson Miller Parameter in Figure 21 with those of NF709R. The latter alloy is a higher chromium version of NF709 with 23%Cr for oxidation/corrosion resistance, similar to a level to that in the development alloys. Rupture stresses for BGA4 lie very close to the mean line although they start to fall away for tests out to longer durations at 700°C. Thus it appears that the upper limit on the service temperature for this alloy will be about 675°C. Tests currently in progress will provide the data necessary data to indicate whether the good short-term behaviour is maintained at longer durations.

Steam Oxidation testing

Samples of the four experimental alloys have been included in programmes being conducted by COST 522 partners, viz. Ansaldo Ricerche, CESI and Alstom Power. Exposures are continuing, but, as may be expected, the performance of all the alloy variants is superior to Esshete 1250.

Hot corrosion testing

The experimental alloys have also been included in a programme looking at hot corrosion (at 700ºC) in a synthetic ash, being performed by Ansaldo Ricerche. Again as expected, behaviour is superior to the original Esshete 1250 alloy.

Overall, properties of the tungsten + copper containing alloy BGA4 look promising for use of the material up to around 675ºC. Testwork is ongoing to provide further confirmation at longer exposure times.

5. STEAM TURBINE GROUP ACTIVITIES

The thermal efficiency of cycles employing steam turbines has increased substantially over the past years, due to items such as increased regenerative heating, introduction of reheat cycles and advances in steam path design, including high efficiency blading. However in order to achieve further advances in efficiency, supercritical conditions are being increasingly adopted. As with components in power plant boilers, reported in section 4, the higher steam temperatures and pressures required necessitate materials with increased creep strength and oxidation resistance. The use of austenitic materials would provide the required properties, however their physical properties such as high coefficient of thermal expansion and lower thermal conductivity lead to very great restrictions in operational flexibility. Consequently the predecessor to this action, COST 501, was focussed on development of ferritic-martensitic 9-12%Cr steels, and the present initiative, COST 522, is concerned with further development of these materials together with coatings and surface treatments.

5.1 Forgings

In COST 501 Round 2, three different alloy types were identified with the potential for meeting the requirements for 600ºC long-term application. The differences to conventional 12% Cr steels were the reduced carbon, chromium and vanadium contents, and additions of niobium and nitrogen. These alloys were of the 9%Cr 1.5%Mo 100ppm B, 10%Cr 1%Mo 1%W, and 10%Cr 1.5%Mo types. Three full sized rotors were produced and fully tested, and based on creep rupture strength the steels provided an increase in application temperature to 600ºC and above, with the boron containing steel showing potential to 620ºC.

For Round 3 of COST 501, analysis of the long-term test data and microstructural investigations led to a further five alloy compositions being defined for 620ºC service. Subsequent production of large trial melts plus extensive testing confirmed that the boron containing steels showed most promise. Two full sized pilot rotors using the chemical composition of FB2 were manufactured and testing on material from these is still continuing.

Even the FB2 material did not appear to approach the potential needed to fulfill the aim of the COST 501 programme successor, which is this present programme COST 522, with a target of 650ºC. Hence further improvement of the ferritic/martensitic grades was required, not only with regard to creep strength but also to oxidation resistance. Consequently, seven trial melts of approximately 150kg were made, forged into bars and heat treated to simulate the core position of a heavy forging. The compositions are given in Table 20. Different heat treatments were carried out to investigate the influence of austenitising temperature on the long-term properties. From the compositions of FB5 and FB6, upscaled melts of 1 tonne were also produced.

An extensive test programme has been performed on the above, including metallographic investigations, short term and long term mechanical properties and oxidation tests, and the testwork was shared amongst the COST partners. Short-term results (tensile and impact tests) are shown in Figure 22. ALSTOM in the UK was involved in creep and fatigue crack growth testing, as follows:

- Creep tests at 625ºC on trial melt FB5
- Creep tests at 625ºC on trial melt FB6
- Long term creep tests at 625ºC on trial melt FB10 (short term creep tests were carried out by ALSTOM Switzerland Ltd)
- Creep tests at 550º and 625ºC on prototype rotor forging FB2P
- Fatigue crack growth tests at 20ºC and 625ºC on prototype rotor forging FB2P

More recently, further tests have been mounted to investigate the long-term influence of improved process routes and heat treatment, viz.:

- Creep tests at 650ºC on FB6AD
- Creep tests at 625ºC on FB8 HTC

After creep test durations of 15,000 hours, the tendency was noted that none of the new melts offered a clear improved behaviour compared to melt FB2. It was concluded that the complex and expensive alloying with cobalt (Table 20) would not fulfil the expectations regarding an increase in creep strength. However, melts like FB6 and FB8, with chromium contents >11% and therefore having an expected improved oxidation resistance, are still better than the 600ºC materials with W and Mo. The plan is to continue the creep testing up to durations of 100,000 hours.

At the beginning of COST, there was only limited experience with the higher boron type alloys. However, during the COST programmes, suppliers have produced large melts with higher boron contents, and forgings have been successfully manufactured, which are still under test. This has given great confidence in the decision that future activities should be focussed on the boron containing steels. A number of compositions for new steels have been designed based on this positive experience, with the contents of Cr, B and N varied systematically as shown in Table 21. The compositions have been manufactured in the form of forged trial melts, and material has been distributed to COST partners for mechanical properties evaluation. Alstom has launched creep tests at 650ºC on the alloy designated FT6.

5.2 Castings

Development of new steels for castings followed quite closely that for forgings, as detailed in section 5.1 above. Two initial alloys were identified, viz. 10CrMoWVNBN and 10CrMoVNbN, and qualified, and such steels are now in use in power plant. The P91 type cast steel G-X12CrMoVNbN 9 1 was qualified within the frame of EPRI Project RP 1403, and, under COST, an attempt was made to further increase the creep rupture strength by increasing C, Cr and Ni contents, adding 1%W and modifying the heat treatment. Trial melts were produced in the form of 100mm thick plates with and without tungsten. Based mainly on the creep tests, the tungsten bearing steel was selected for the production of a 5 tonne valve body. Sections with different wall thicknesses were extensively tested, including fabrication welds. Creep tests have reached more than 82,000 hours, and the temperature for 100 MPa at 100,000 hours appears to be around 593ºC.

For 620ºC service (COST 501 3rd round), extensive microstructural investigations allowed further compositional modifications to be made to produce five trial melts which were cast as up to 200mm thick plates or 500 mm thick stepped blocks. The melts were designated:

CB1 G-9.5Cr 1.5Mo 1Co B N (40 ppm B) (Stepped block)

CB2 G-9.5Cr 1.5Mo 1Co B N (110 ppb B) (Plate)

CD2 G-9.5Cr 2W 0.5Mo 1Co B N (Stepped block)

CE2 G-9.5Cr 1W 1Mo 1.5Co B N (Plate)

CF2 G-9.5Cr 1.5Mo 1Co N

The test programme is completed on these, except for long-term creep tests, which have reached more than 60,000 hours. With respect to creep strength, CB2 and CD2 show promise, offering an improvement in creep strength. Additional tests for CB1heat treated at the same austenitising temperature as the remainder (as this alloy was tested initially after a 50ºC lower austenitising temperature) have also been started within the subsequent COST 522 action.

Under COST 522 itself (the present action), as for the forgings, further improvement was required in both creep strength and oxidation resistance to attempt to achieve the 650ºC target. Six cast trial melts were produced as plates 100mm thick, based on the CB2 composition, and compositions are shown in Table 22. An extended programme was performed including metallographic investigations, short and long term mechanical properties, oxidation testing, evaluation and qualification of filler metals and the investigation of production welds on the components. E.ON (formerly Powergen) has been actively involved in the mechanical testing of a 9Cr1.5Mo1Co cast valve body material (CB2), from pre-production and trial valve body castings, in the as-received and artificially aged condition, to provide data for structural integrity assessment for both new and service exposed plant. The data obtained are those which would be required for the integrity assessment of plant in flexible operation. A range of data has been obtained including tensile, stress relaxation, cyclic stress-strain, low cycle fatigue crack initiation, fatigue and creep crack growth.

ALSTOM in the UK was involved in creep testing, as follows:

Creep tests at 600º, 625º and 650ºC on prototype valve chest CB2P, location A

Creep tests at 625ºC on trial melt CB5

Creep tests at 625ºC on trial melt CB1HT2

Creep test times to date range from 12,000 to 20,000 hours, and as for the forging material trials, none of these cast trial melts are showing a clear advantage over the CB2 alloy at higher temperatures. This has led to the design and production of new melts with nominal compositions as for the forging materials, shown in Table 21, i.e. with B in the range 100-300 ppm, no Co or W addition, and Mo at 1.5%. Again as with the forging materials, these have been distributed to COST partners for evaluation of mechanical properties. Alstom have launched tests at 650ºC on trial melts CT3 and CT7.

5.3 Bolting

The activities in this section of the Turbine Group are concerned with the development of improved alloys for high temperature bolting, and focussed on two alloy systems. An improvement was sought in the 9-12%Cr type alloys, based on results from previous work and on an improved knowledge of microstructural behaviour, and suitable nickel based alloys were selected and procured from materials commercially available but whose suitability for turbine bolting had not been demonstrated.

5.3.1 9-12%Cr Alloys

The current ferritic/martensitic alloy steels for bolting applications in high temperature steam turbines are X19CrMoNbVN11.1 (X19) and 1% CrMoV (Durehete 1055). X19, with the higher chromium content, offers a potential base for development to higher strengths at 580 - 620°C. The creep strength of X19 depends on the precipitation and stability of various carbide/nitride species involving chromium, molybdenum, niobium and vanadium. Previous thermodynamic studies have indicated that increasing nitride precipitation, through the use of higher nitrogen levels, may promote improved long-term high temperature properties. However, there is a limit to the amount of nitrogen which can be retained in (solid) solution during steel making and subsequent processing and hence be available for precipitation as nitrides during heat treatment and service.

A programme of work was initiated by Corus to identify optimum levels of nitrogen, consistent with the requirements of processing/processing, for improved creep and stress relaxation properties using X19 as the base composition. An air induction melted laboratory cast was made following initial experimental activities to evaluate three 25kg air induction melted casts which contained nitrogen levels between 0.06 – 0.15%. This new cast was split into two 25kg ingots with nitrogen levels of 0.10% and 0.13%. Cast analyses are given in Table 23 along with specified element ranges from BS EN 10269: 1999 for steel no. 1.4913 (X19). Ingots were forged to 50mm square section, rolled to 20mm diameter bar and sawn lengths heat treated.

Quality assurance procedures were applied both before and after heat treatment (using ultrasonic testing and alternating current potential drop testing respectively), to detect the presence of any internal or surface cracks. Following detection of the latter, for the 0.13%N cast, modifications were made to the process route to reduce the risk of further cracking in subsequent rolling of test material.

A room and elevated temperature mechanical test programme was carried out, and room temperature tensile and impact properties for both casts met the requirements specified in BS EN 10269: 1999 for steel no. 1.4913 (X19). A comparison of tensile test data for the two alloys revealed lower 0.2% proof strength and tensile strength values for the higher nitrogen cast (H1F30) at both room temperature and 600°C. This was thought to indicate incomplete solution of nitride precipitates during solution treatment, leaving relatively coarse undissolved precipitates which would be ineffective for improving strength. In addition, they reduce the available nitrogen for solid solution strengthening and for producing a fine precipitate dispersion on tempering.

Stress rupture testing was conducted on both plain and notched specimens of both alloys at 550, 575 and 600ºC, and these tests are ongoing. At each of the three test temperatures the lower nitrogen cast gave longer plain rupture lives. It is apparent, therefore, that raising the nitrogen level from 0.10 to 0.13% (the latter above the top end of the range permitted (0.10%) in BS EN 10269 for X19) was detrimental to the plain rupture strength in the two alloys assessed. No clear effect on notched rupture strength could be established. The nitrogen levels in both casts are well above the level of 0.05-0.06% found in normal production material.

There was no significant difference between elongation and reduction of area values for the plain tests for the 0.10 and 0.13% nitrogen alloys.

A comparison of plain to notched rupture lives for completed tests at each of the three stress levels at 550°C and 575°C respectively showed the higher nitrogen cast to be notch strengthening whereas the lower nitrogen cast was notch weakening. At 600°C, both alloys were notch strengthening although this is based on a single stress level (200MPa) only. The notch strengthening behaviour of the high nitrogen cast was a result of the low plain rupture lives exhibited by this alloy rather than being an indication of good notched rupture strength.

Stress relaxation tests are being carried out at 550°C and 0.20% strain. The testing has so far reached just over a third of the 30,000 hour aim life. Test data for the higher nitrogen alloy lie on or slightly above the X19 mean line. Stress values for the lower nitrogen alloy showed a sharp drop between 1,000 and 2,000 hours, however there has been little further drop between 2,000 to 10,000 hours by which time the residual stresses in both alloys were similar and close to the mean line for X19. Continuation of testing for both alloys up to the 30,000 hours maximum duration given in BS EN 10269 will provide data to establish trends for the stress relaxation behaviour above 10,000 hours.

5.3.2 Nickel Based Alloys

Alstom co-ordinated and contributed to investigations to develop a Ni-based bolting alloy with a coefficient of thermal expansion matching that of the 9-12%Cr steels. The work built on the earlier progress made in COST 501. Two alloys were investigated: Haynes 242 and 783.

Alstom investigated alloy 242 through metallography, determination of the thermal expansion coefficient, tensile and relaxation testing. It was found to have poor relaxation strength therefore additional development was abandoned.

In COST 501, alloy 783 had been found to be notch weakened in creep tests. However the supplier, Special Metals, reported improvements in the manufacturing process and advised notched rupture test results indicating freedom from notch weakening. Therefore further plain and notched rupture testing was carried out and this confirmed Special Metals‘ results.

A 2- phase development programme was then launched.

1. Special Metals provided 54mm bar which was investigated as follows:
   Manufacture of full scale bolts by Hydratight Sweeney
   Relaxation testing of these bolts in flange assemblies by Hydratight Sweeney

Tensile testing by ALSTOM
Survey of hardness, grain size and microstructure by ALSTOM
Uniaxial relaxation testing by ALSTOM
Oxidation testing by NPL

The results of these tests confirmed the properties of 783 as being suitable for steam turbine bolting and demonstrated the application of the alloy to bolting.

2. Characterisation through tensile, relaxation, rupture, ageing and stress corrosion testing of a larger diameter bar to underwrite application of the alloy to larger diameter bolting. Material of 100mm diameter was supplied for this programme but after a screening programme by ALSTOM including tensile and notched rupture testing and metallographic examination it was concluded that the material was not representative of best manufacturing practice. Further work was therefore cancelled. Currently the procurement of additional material from Special Metals is being considered.

6. COMMON ACTIVITY GROUPS

6.1 CA2 Welding

UK organisations involved in this group were ESAB, TWI and Metrode.

The work done by Metrode has already been covered as part of the Boiler Group work under items 4.1.3, 4.2.2 and 4.2.3.

6.1.1 ESAB

Of the new steels, which are being developed for improved performance over P91, it is not clear which will be widely adopted and what the requirements will be for welding consumables. A programme of work was therefore planned, based on reported developments in parent materials; to see which additional strengthening mechanisms are applicable to weld metals and how any adverse changes in toughness and other properties could be minimised. In the first two phases, 24 experimental consumables were made in which chromium, molybdenum, cobalt, tungsten, titanium and boron were varied in a statistically designed experiment. The ranges of these elements tested are as follows: Cr 9.4-12.5%, Mo 0.25-1.25%, Co 0-3.0%, W 0-1.0%, Ti 0-0.15% and B 0-0.04%.

In addition, wires with compositions close to those of P91, P92 and two more parent steels were made as benchmarks.

Mechanical properties were measured on the consumables at room temperature, and the ranges of proof strength (579-793 MPa) and tensile strength (702-932MPa) were high compared to those of most materials in the programme. At the same time, toughness was relatively poor. As most of the materials are operating in a regime where strength and toughness are inversely related, it seemed likely that the toughness would be improved by a PWHT designed to soften the weld further.

Regression analysis of yield strength on wire composition gave an equation related to Ti and B contents. If metal composition rather than wire composition is used, this dependency changes to Si plus B.

From initial results from the first 18 wires, a regression equation showing adverse effects of Cr, Ti and B on toughness was derived, but as only two Charpy values above 30J were measured, the analysis was not entirely convincing. The same regression was performed on the complete data set when it became available, and a similar result was obtained in which the coefficients for Ti and B changed but the spread of values gave greater confidence in the analysis, Figure 23. The fact that Ti and B were both shown to be strengthening elements suggested rerunning the analysis with proof strength included, and when this was done, Ti dropped out of the regression equation (Figure 24). This in turn suggested that the embrittling effect of titanium is due to its dispersion hardening effect, as in other weld metals, whereas that of chromium and boron is additional to any hardening effects they may have.

Second order terms were tried in the regression and gave an indication that the effect of titanium could be mitigated at higher chromium levels, but the overall performance of the regression was barely improved.

The analysis was then repeated using weld metal compositions instead of wire compositions. Using only the elements that were deliberately varied, for the pooled data the regression equation was a function of Cr and B only (and these had adverse effects).

As in the case of the analysis of strength, the absence of titanium from the significant effects is surprising at first sight. Unfortunately, in the process of metal transfer across the arc and in the slag-metal reactions which take place, many interactions between the independently varied elements and others occur so that the data becomes much more difficult to interpret. The overall conclusions from this part of the work were that alloying with titanium and boron was associated with reduced metal toughness. Chromium and nitrogen are also implicated in weld toughness reductions. Although nitrogen did not form part of the experimental design, there was a small amount of random variation in the levels achieved and this was sufficient to reveal its adverse effect on toughness. Such an effect has been shown in a number of previous investigations at ESAB. No adverse effect of molybdenum, cobalt or tungsten has been detected.

The work on weld metal toughness did not absolutely rule out any particular approaches to alloying, but there was a clear suggestion that titanium and boron would be least preferred if high temperature properties could be achieved by other means.

With regard to Post Weld Heat Treatment (PWHT) of the 9-12%Cr steels, the presence of a range of secondary hardening elements ensures that significant changes in mechanical properties can occur within the range of heat treatments that users might wish to apply, and which will partly be determined by the form and history of the base material and the nature of the component being welded. It became apparent during the present programme that there was no uniformity in heat treatments being applied, so it was difficult to make comparisons between results from different projects. It was therefore considered useful to carry out some experiments to look at the effect of PWHT. Wires CST25 and CST26, corresponding approximately to P92 and E911 steels, were chosen for these tests.

Welds were fabricated and heat-treated at 730ºC, 745ºC and 760ºC for times of 1 and 12 hours. Hardness traverses were carried out at mid-thickness across the weld and Charpy specimens were prepared from the welds and tested. Summaries of the effect of PWHT temperature on weld metal hardnesses for each of the weld types are shown in Figures 25 and 26, and effects on toughness in Figures 27 and 28.

The standard post weld heat treatment for the welds in this project was 2h at 760°C, and the room temperature tensile properties of the welds were on average higher than those of most parent materials they would be required to weld. Tests with alternative treatments showed that a longer time at temperature, by softening the weld, could greatly improve the toughness even with lower PWHT temperatures. There has been a tendency in recent years to reduce the temperature at which welds are heat treated, to as low as 730°C in the case of P91 weld metal. This improves creep rupture strength in very short tests, but the evidence from the COST programmes and elsewhere does not confirm that it improves long-term properties. If more highly alloyed materials are introduced, it may be that a different approach to PWHT will be needed if weld metal toughness is to be acceptable.

6.1.2 TWI

For increased service temperatures there are a number of alloys which have been developed, typically containing 9-13%Cr, ~0.5%Mo and 1-2%W, with additions of Ni, Nb and V. Whilst welding consumables are available for these alloys there is a need to understand more fully the role of composition in the microstructural development and mechanical properties of weld metals. This programme of work aimed to explore the possible toughness improvement in weld metals for the W-containing steels NF616 and HCM12A through variations in the deposit chemistry.

Earlier TWI studies on weld metals for grade 91 [7] showed that the addition of ~1%Ni, in combination with reduced Si, Nb and N, improved toughness.

A further TWI study on grade 91 weld deposits suggested that the addition of Co, like Ni, was beneficial in reducing δ-ferrite (although its effect was less potent than that of Ni), and it improved toughness [8]. However, unlike Ni, Co does not significantly affect the Ac_1 temperature. Tungsten has been added to the new generation of 9-13%Cr steels to improve creep resistance and high temperature strength, albeit with a small reduction in elongation. However, it is a strong ferrite former, and promotes the retention of δ-ferrite. The addition of 1%Ni or 2%Co, in combination with 1%W alloying, was sufficient to suppress the δ-ferrite retention, and improve Charpy toughness [8].

The starting point was the current 'commercial' Manual Metal Arc (MMA) electrodes for each material, and four different variations for each material type, in the form of 4.0 mm diameter electrodes, were provided by Metrode. The parent steels were HCM12A (Sumitomo Metal Industries) and NF616 (Nippon Steel Corporation), and a multipass MMA weld was produced for each of the electrode types using 1m long strips of parent material. Descriptions and compositions of the weld metals resulting are given in Table 24.

Metallography and hardness tests were performed on as welded samples and after Post Weld Heat Treatment (PWHT) of 760ºC. An all weld metal tensile specimen was machined from each deposit and tested at ambient temperature.

The former indicated that the compositional variations did not appear to have lowered the Ac_1 transformation temperature to a level below the PWHT temperature of 760ºC. The compositional variations did not significantly affect the transformed microstructure, and in all cases the amount of δ ferrite was very low. Earlier TWI work on modified 9%Cr-1%Mo weld deposits suggested that no appreciable δ-ferrite would be retained for chromium equivalent (Cr_{eq}) values less than 8 [8]. It appears that this statement is equally valid for the current W-containing deposits, which all had Cr_{eq} values of <7.5.

Hardness results are given in Table 25, and tensile data in Table 26. In general, the Vickers hardness data supported the microstructural observations showing only limited variation within and between the two series of deposits. For both the 9%Cr and 10%Cr series, the addition of 1%Co to the base-line deposit generally gave a hardness and strength increase after PWHT that was lower than other deposits in the series. For both deposit series, the base-line deposit exhibited the highest hardness after PWHT. This can, at least in part, be explained from the minor compositional variations, mainly the higher levels of C, Mn and W. For both series, the limited tensile data, and the inevitable scatter, do not reflect any further trends for 0.2% proof strength or tensile strength with changes in composition. In all cases the values recorded exceeded the ASME Code Case requirements.

Standard Charpy specimens were machined from 2mm below each of the root and cap surfaces, and tested over a range of temperatures to produce transition curves.

Eight single-edge-notch-bend fracture mechanics specimens were extracted from each panel, pre-fatigued as required, each specimen tested in three-point-bending, and the fracture toughness calculated in terms of crack-tip-opening-displacement (CTOD).

The Charpy transition temperature data (based on the best-fit and lower bound curves) are summarised in Table 27, and the transition temperature data, on the basis of the temperature to achieve a CTOD of 0.1mm, in Table 28.

The data sets have been analysed using regression analysis to look at the effect of composition on toughness. The highest toughness after PWHT for 2 hours at 760ºC was obtained for the addition of 1%Co to each of the baseline weld metal compositions. The toughness of the W-containing weld deposits was consistently inferior to the W free deposits studied earlier.

Limited creep rupture testing was conducted, as it was possible to machine only two creep rupture specimens from each weld metal, but in addition cross weld specimens from W13 and W18 were obtained and used for scoping tests.

The baseline compositions in both the 9%Cr and 10.5%Cr alloys had the lowest creep rupture strength. For the 9%Cr weld series, all the changes in alloying improved the creep rupture strength, the best being the alloy W13 with 1% Ni and 1% Co. In the 10.5%Cr welds, the best creep rupture strengths were found in the W16 (base +1%Co) and W19 (base -Ni+3%Co) welds.

After reviewing previous Charpy and CTOD results, and the short term stress rupture results above, the initial conclusions are that the compositions of welds W12 (9%Cr baseline +1%Co) and W16 (10.5%Cr baseline +1%Co) merit consideration as consumables for welding high Cr steels. Longer term creep rupture testing of these is required. Oxidation and corrosion problems limit the temperature of use of 9%Cr steels to 625ºC [9]; hence for service at 650ºC the higher chromium alloys are preferred. Thus the deposit containing 1%Cr (W16) is potentially the composition of greater interest, for welding 10.5 to 13%Cr steels.

6.1.3 Microstructure Modelling of Ferritic/Martensitic Steels

This work was conducted by Loughborough University under the auspices of both the COST 522 Boiler Group, and here in Common Activity Groups. It is intended to improve the understanding of the microstructures developed in weld metals, as against the homogeneous parent materials, by examination of typical welding microstructures and their modelling from first principles. From such an improved understanding, it should be possible to develop better, optimised consumables for use with the current advanced steels and to further the more rapid development of welding consumables for newer variants of the advanced alloys.

The microstructure feature initially studied was the formation of delta ferrite and how this was influenced by the weld metal composition covering a range of Cr contents from 8 - 12 % and with additions of Cu, Co, Mo and W (see Table 14), the experimental alloys also used by Metrode above, see section 4.2.3. All the variants were changed in a systematic manner in order to check the susceptibility to delta ferrite formation. The materials were produced as weld beads coming from multi-pass welds on a P91 grade substrate.

The modelling of the formation of the delta ferrite- austenite mixture in weld metals in terms of Cr^* and Ni^* equivalents was performed by means of MTDATA. A special procedure to estimate the efficiency of alloying elements such as Mo, W, V, Nb, Mn, Co, and Cu in stabilizing delta-ferrite or austenite was developed. The procedure was based on the ability of MTDATA to calculate different versions of constitutional diagrams when a variable concentration of a second element is changed.

The initial results helped to identify the effects of composition on delta ferrite formation in the weld deposit. There is a clear difference between the delta ferrite distribution in the outer and centre parts of the weld bead, suggesting that thermal history is important. The thermal history is clearly different in material that has undergone several thermal cycles. There is blocky delta ferrite in the last pass weld material whereas smaller, necklace type particles associated with grain boundaries are present in the central weld metal.

Wagner’s theory of diffusion phase growth was used to analyse the process of delta-ferrite decomposition in the centre bead of weld metal. Modification of Wagner’s theory allowed the description of delta ferrite content as a function of steel composition. It was shown that Cu accelerated the process of delta-ferrite decomposition, rather than Co and Ni, and hence steels doped with Cu could have a higher concentration of Cr, which would allow an improvement in service properties such as resistance to oxidation.

It is realised that none of the mathematical manipulation is shown above. It is most difficult, however, to reproduce in a meaningful manner, only part of such a treatment, and reproduction of the somewhat lengthy complete treatment is inappropriate in the present report, which is a summary of the results of 15 projects. Accordingly the reader is directed to references [10, 11], which cover the work in more detail.

6.2 CA3 Metallography and Alloy Design Sub Group

The work of this group was led and co-ordinated by Alstom.

Prior to the third round of the COST 501 initiative, which started in 1993, knowledge of the microstructure in advanced 9-12%Cr steels and its evolution was relatively sketchy and qualitative. Nevertheless, the two earlier rounds of COST 501 did involve a large amount of empirical work applied to the development of improved alloys, the results of which were applied to the manufacture of prototype turbine rotor forgings and valve chest castings. These early developments were not based on any fundamental considerations of microstructure or creep mechanisms, but still they produced two improved alloys for rotor forgings (designated steels E and F), and an improved casting alloy (CT) that were employed successfully in power stations.

In the third round of COST 501, and subsequently this current project COST 522, far more detailed microstructural investigations were possible and indeed were carried out, both on newly designed alloys and, possibly more importantly, on materials from the earlier phases which had by now accumulated significant time and temperature exposures. The following parameters were investigated: hardness, grain size, primary phase description (phase type and chemical composition), secondary phase description (species such as $M_{23}C_6$, MX, Laves phases etc., size distribution, location, chemical composition, inter particle spacing), dislocation structure (sub grain size and shape, dislocation density). Many sophisticated detection, identification and measurement systems were employed, and the observations enabled significant insights into the microstructural evolution of the steels under consideration and its relationship with mechanical properties. In addition to these microstructural investigations, COST 501 also included the development of models to predict both microstructure and the properties which arise. A fuller description of the history outlined above is given in reference [12].

The success of these studies was carried forward into the latest work under COST 522, where a group of 21 partners worked on a series of parallel projects to investigate different aspects of microstructural development. The work involves investigations of more recent alloys developed in COST 501, new alloys being developed in COST 522, and commercial alloys such as P92 and P122. Modelling studies include further work on the kinetics of second particle precipitation, growth and coarsening, including an extension of the model developed by Robson and Bhadeshia [13] which predicts the sequence in which phases precipitate, their fraction as a function of time and the distribution of particle size for each phase. This is being applied to advanced austenitic alloys.

The objective of alloy design is to define a composition and heat treatment which leads to a material meeting several requirements:

High long term creep strength with resistance to isothermal softening and embrittlement.

Resistant to the plant environment, e.g. steam, flue gas.

Capable of manufacture in economic product forms which are ultrasonically inspectable.

Weldable, where appropriate.

The evidential bases used in the alloy design philosophy are explained in detail in reference [12]. The insights into optimum microstructure from the above have formed the basis of the alloys being investigated in COST 522. These include, e.g., the separate and combined effect of adding boron and nitrogen, and the difficulties with segregation of boron. The enhancement of creep strength with vanadium, but the adverse effects of the formation of Z phase which is encouraged by high V levels. Increased creep strength from higher solution temperatures, but at the expense of coarser grain size. Increase in oxidation resistance from increased chromium, but this may also lead to delta ferrite formation.

Taking these factors into account, the martensitic alloys for forgings listed in Table 29 were designed for investigation in the COST 522 Turbine Group. Higher Cr levels are investigated for improved oxidation resistance and two carbon levels are used to explore the optimum level for carbide formation. Additional Co was added in one variant to investigate the potential of Co to reduce diffusion rates by raising the Curie temperature. Small amounts of W were added to two melts to investigate solid solution strengthening at low levels. These alloys were, and still are (as ongoing tests) being investigated in both cast and forged product forms as indicated in earlier sections of this report.

COST 522 builds on the previous experience of COST 501 also in the application of advanced methodologies, such as Energy Filtered Transmission Electron Microscopy (EFTEM), which enables a much more rapid and rigorous analysis of secondary particles, Atom Probe Field Ion Microscopy to identify distributions in individual particles, and Secondary Ion Mass Spectrometry (SIMS) which has been applied for boron mapping within grains and sub-grains. Modelling methods have been improved and extended to apply to advanced austenitic boiler tubes (14- see 6.2.1 below), kinetic models developed to predict delta ferrite formation in welds (see section 4.2.4), and modified thermochemical parameters developed to correct Thermocalc predictions of the Laves phase solvus temperature, which were lower than observed experimentally.

The consensus view on key aspects for design of high temperature 9-12%Cr martensitic alloys has been reinforced, and can be summarised as follows:

<u>For high creep strength</u>, requirements are for a fully martensitic structure, a dispersion of $M_{23}C_6$ carbides to stabilise sub-grain boundaries, a dispersion of MX particles to inhibit dislocation movement within sub-grains, and addition of boron to stabilise the carbide structure.

To avoid degradation of properties during long term service requires freedom from precipitation of Z-phase, M_6C and M_2C, achieved either through design of the thermodynamic equilibrium to ensure such phases are not present or through designing the steels so that these phases are kinetically inhibited over the lifetime of the power plant.

6.2.1 A Neural Network Model of the Creep Strength of Austenitic Stainless Steels

One major difficulty in trying to predict the long term properties of austenitic steels is the strong influence of alloying elements and their numerous interactions. This explains why most of the empirical approaches are restricted to limited ranges of compositions. Neural networks represent a more general regression method, which ameliorates most of the problems encountered by linear regression methods. In this present study, conducted at Cambridge University and part supported by Innogy plc, neural network analysis was applied to a database covering a vast range of compositions of austenitic stainless steels to estimate the creep rupture life and the creep rupture stress as a function of a number of parameters. It was concluded that the potential of the method was clearly illustrated in its ability to perceive interactions between the different input variables. Predicted trends were found consistent with those expected and the quantitative agreement was frequently satisfying. The method can be applied widely because of its capacity to indicate uncertainty, including both an estimate of the perceived level of noise in the output, and an uncertainty associated with fitting the function in the local region of input space.

A full description is given in the author's PhD thesis (Thomas Sourmail), which can be found in Reference [14].

6.3 CA4 Oxidation and Protective Systems

Alstom provided industrial steering to the activities of the Oxidation and Protective Systems group, which involved a number of partners in continental Europe. The activities of these partners are listed in Table 30. Tables 20 and 22 give the chemical compositions of the steels for the wrought (FB series) and the cast (CB) series which were tested; these were the materials used in the steam turbine activities under sections 5.1 and 5.2 above. A benchmark P92 control material used by all partners was also included.

The conclusions from the work were as follows:

1. There was fairly good agreement between the results from the different participating laboratories in short-term exposures in steam. The tendency for spalling led to somewhat larger scatter of the data after longer exposure times.
2. Chromium and silicon have a major influence on the kinetics of oxidation. Chromium contents greater than 11% and silicon contents greater than 0.3% lead to significant reductions in the rate of oxide growth.
3. Unresolved issues concern the effect of steam pressure and the tendency of the oxide scales formed in steam to spall.
4. There is promising potential for the application of coatings to enhance the steam oxidation resistance of Cr steels. Further development is required to optimise the processes for large components and to investigate the effects of the coating on mechanical properties.

The contributions of NPL to the Oxidation and Protective Systems Group were on the subjects of characterisation and modelling of spallation of oxide scales, and metal wastage rates in furnace wall materials, and these are covered in some detail under the Plant Integration Group report below (sections 7.2.1 and 7.2.2).

Since the UK involvement by NPL is detailed elsewhere in this report, and that by Alstom was limited to co-ordination of the group, all the other experimental work was performed by the partners from continental Europe, and as such is not really appropriate to being reproduced in this report. However, a detailed summary can be found in reference [9].

7. PLANT INTEGRATION AND ANCILLARY COMPONENTS GROUP

A number of projects were conducted under the auspices of this group, all directly or indirectly concerned with corrosion.

Cranfield University's activities were concerned with the performance of materials in heat exchangers operating in a co-fired boiler. They were carried out by exposing candidate materials a) within controlled atmosphere furnaces, and b) to simulated furnace wall and superheater corrosion environments in a 150 kW combustion test facility, employing coal and biomass co-firing.

NPL carried out steam oxidation testing in flowing steam in a laboratory test rig, and developed a model to predict the onset of scale cracking and spalling. In addition, metal wastage rates in candidate furnace wall materials were determined in simulated low NOx combustion atmospheres.

E.ON (formerly Powergen) conducted corrosion testing in simulated furnace wall corrosion environments in a $1MW_{th}$ pulverised coal Combustion Test Facility. In addition, long term tests were carried out using air cooled corrosion probes in three superheater/reheater locations in an operating utility boiler, followed by measurement and analysis of results.

Mitsui Babcock looked at the integrity of HVOF coatings under creep and thermal cycling conditions, and also performed some simple air atmosphere tests on coated coupons covered with synthetic deposit, for comparison with the simulated atmosphere tests performed by other partners.

More details of the above testwork are given below.

7.1 Cranfield University

There is growing interest in the use of biomass in existing power generation systems as a relatively easy method of introducing significant quantities of renewable CO_2 - neutral fuel. Co-firing of biomass with coal is an effective way of introducing biomass into the power production chain. Existing coal-fired power stations are both larger and more efficient than potential new biomass power plants, so a few percent of biomass feed into an existing large coal fired station could give more biomass derived power than a new dedicated biomass station. However, for the existing coal fired stations, this gives some potential practical problems, viz.:

- the control of co-firing two fuels
- changes to bottom/fly ash chemistry
- changes to deposition (fouling and slagging) within the boiler
- reduced reliability of key high temperature components due to increased corrosion problems relative to those experienced with coal alone.

Hence this project was aimed at investigating the effects of a range of different potential exposure conditions on the corrosion of candidate heat exchanger materials. The first, (and a continuing) part of the project was to gather information on potential European biomasses, and this extended to using more than 400 sources. A survey of deposit compositions in co-fired combustion systems followed on from this, which considered the effects of the following on deposit formation:

- sodium/potassium, alkali/silicon and chlorine/sulphur ratio of fuels and within the combustion gas stream (where this information is available)
- fuel combustion temperatures
- heat exchanger surface temperatures
- heat exchanger local gas – surface temperature differences

The test work was carried out using both laboratory investigations, and by modifying an existing combustion pilot plant to handle biomass fuels and extend the range of combustion gases which could be used for materials exposure, followed by test exposures.

For the laboratory tests under co-firing conditions, the materials studied were 1%Cr, 2¼%Cr, X20CrMo121, AISI 347H, and Alloy 625. Two gas compositions were used, both with nominally 1420 vpm SOx, 320 vpm HCl, 14%CO_2, 6%H_2O, with one also containing 4%O_2 0%CO whilst the other also contained 0.1%O_2 4%CO, balance N_2. Eight deposit compositions were employed comprising different relative mixtures of KCl, K_2SO4 and pulverised coal fly ash, each relevant to a particular temperature/material/gas composition. Four tests were run for 1000 hours each at temperatures of 425, 560 and 600ºC, as shown in Table 31.

The performances of the materials were determined by dimensional metrology to give distributions of metal losses, according to [15], as required for incorporation into the database of materials corrosion performance and used in the subsequent materials performance modelling activities [16, 17]. All the corrosion damage measurements were processed so that the data sets were ordered from the most damage to the least. This enabled corrosion damage versus probability plots to be constructed to show the sensitivity of the corrosion damage to changing gas composition, alloy or deposit composition (e.g. see Figure 29). One damage level was then selected for comparing the performance of all materials and exposure conditions (damage with a 10% probability of being exceeded).

The data were used to derive empirically based corrosion models of the materials corrosion performance under the above test conditions. Figure 30 illustrates the correlation between predicted and measured corrosion rates for the models.

Results showed that there were increasing levels of corrosion damage with:

- Decreasing alloy chromium content
- Increasing temperature

- Increasing levels of K_2SO4 + KCl in the deposit
- Higher ratios of KCl/K_2SO4

Coal and biomass co-firing was performed in the 150kW combustion test facility at the Power Generation Technology Centre at Cranfield University, modified, as indicated above, to handle biomass fuels. Exposure conditions can be set to be representative of those found in large-scale power plants. The use of real fuels in this test rig (Figure 31) enables continuous deposition of ash and condensation of vapour phase species, as well as the simultaneous use of realistic levels of gaseous species. In addition, cooling of the probes results in heat fluxes through the samples. All these factors improve the confidence that results from this type of test facility will be closer to plant behaviour than most laboratory tests.

The following fuel mixes were employed: coal with normal operation, coal with low NOx operation, coal-20% straw and coal-20% wood. Tests were performed for 50-100 hours with the materials and target temperatures as shown in Table 32.

With regard to deposition during the testing, the deposit compositions found from the co-fired tests were not significantly different from those found in the coal-fired tests. Given the composition of the willow wood, this was to be expected from the analysis carried out earlier in the project. However, for the straw it had been expected that KCl would be released in the fluidised bed combustor. It was considered that the unexpectedly low Cl content of the straw used in these tests, combined with the mixing of the FBC product gases with the burning pulverised coal in the top-up burner, was sufficient to shift the balance towards that seen in pulverised fuel burning alone (i.e. any KCl present was converted to potassium silicates and sulphates, the chlorine went to HCl and so no KCl was found in the deposits).

Materials performance was determined by dimensional metrology before and after exposures as detailed in (16). Initial inspection of sections through the samples showed relatively little damage on most samples, in line with expectations from the deposition observed. The metrology data confirmed the low damage levels observed. To reduce the quantity of data that was being handled and for comparison with other materials performance data, it was decided to extract the damage measurements with a 10% chance of being exceeded for every sample measured, as was done for the laboratory tests above. The corrosion rates found from the firing tests with 20% straw were in line with those found for wood or coal firing alone.

7.2 NPL

7.2.1 Characterisation and Modelling of Spallation of Oxide Scales

Oxide cracking and spalling of a protective oxide layer formed by steam oxidation can lead to greatly enhanced metal loss. NPL have developed a model of scale failure by cracking/spallation, and applied the results of steam oxidation tests to validate this model.

Specimens of P92 steel were oxidised in flowing steam at atmospheric pressure at 600 and 650ºC for times up to 2000 hours. The specimens were then cooled at a linear rate of 100 C/ hour whilst being monitored for acoustic emission (AE). A typical AE record during cooling is shown in Figure 32. Two distinct peaks in AE activity are observed, the first of which is interpreted as the initial cracking of the oxide scale and the second as the actual spallation event.

Metallography on the cooled specimens revealed the existence of a three layered haematite/magnetite/spinel oxide with underlying internal oxidation of the substrate. The most common type of failure event in the oxide was through thickness cracking in the magnetite, but buckling in the haematite (from compressive strain) and shear cracks in the spinel were also seen.

The model used was based upon a concept that was originally developed to predict tensile cracking in polymer composites. The basis of the model, when applied to multi-layered coatings, is to divide the specimen into several layers representative of the geometry of the system that is being modelled. Each layer in the system is attributed specific properties characteristic of the material in that layer. Analytical methods of solving the linear elastic stress analysis problem are used to predict the stress and displacement distributions everywhere in each layer of the system. Numerical methods are needed to solve the fourth order ordinary differential equations that govern stress transfer between layers in the presence of cracks. Comparing model predictions with the results of FEA has extensively validated the modelling technique. Energy methods that are fully consistent with linear elastic fracture mechanics are then used to predict the conditions of loading for which it is energetically favourable for cracks to form in specific layers. Ultimately, progressive loading of the system leads to the through-thickness cracks initiating delaminations and spallation along the interface.

During cooling, stresses in the oxide scales are generated due to the different thermal expansion coefficients of each material layer. Thermal expansion coefficients as a function of temperature for haematite, magnetite, spinel and 9Cr1Mo steel have been collated from the literature [18, 19] and are presented in Figure 33. It can be seen that haematite and the substrate, having the lower coefficients of thermal expansion than the other layers, will tend to be subjected to compressive stresses during cooling whilst the magnetite layers, having higher thermal expansion coefficients, will be subjected to tensile stresses during cooling. The spinel layer may be subjected to either tensile or compressive stresses depending upon the relative influence of the magnetite and substrate surrounding it.

Elastic parameters for the layers, taken from the literature (except for Young's modulus of the spinel, which was measured by nanoindentation during the course of this work), are shown in Table 33. In this preliminary modelling activity these parameters have been taken as independent of temperature as any effects of temperature dependency are expected to be minor.

During a simulated cooling test of 100ºC/hour, a fracture energy was assigned to the magnetite layer whose value predicted the experimental first crack observations. As at this stage the model is not capable of predicting interfacial crack growth and final spallation, a pragmatic criterion for the latter was adopted, viz. that spallation occurred after a further 200ºC temperature drop after first cracking of the magnetite.

Observations of scales formed during a series of exposures at 600ºC for up to 2,000 hours had led to the development of a set of rules for the evolution of the individual layers within the scale with time, viz. i) the outer haematite layer remains at a constant thickness of 4.7µm, and ii) the magnetite and spinel layers grow at rates such that the ratio of their thicknesses remains constant at 1.05. Using these rules, model predictions of the temperature drop to initiate cracking and spallation of the magnetite as a function of total scale thickness, after oxidation at 600ºC and cooling at 100ºC/hour have been made. These are shown in Figure 34, together with data from controlled cooling tests. It can be seen that the model represents an adequate description of this limited dataset although further refinements to the model, e.g. fitting the model to one of the other data points to obtain a slightly different (higher) value for fracture energy, would improve the overall fit.

A more detailed treatment of this work can be found in Reference [20].

7.2.2 Metal Wastage Rates in Furnace Wall Materials

NPL investigated metal wastage rates of the furnace wall materials T22 and T23 under simulated low NOx combustion atmospheres at 440 and 540 °C. A deposit of composition 60% FeS 40% Fe_3O_4 was coated on some specimens. The maximum duration was 3000 h.

The work showed several systematic trends as the temperature, gas composition and deposit were varied. Figure 35 demonstrates the influence of oxygen content and presence of deposit on metal wastage of T22 at 440°C. In the absence of both oxygen and a FeS/Fe_3O_4 deposit the metal loss kinetics are linear whereas if oxygen, deposit or both are present the metal loss kinetics are parabolic. This behaviour is replicated at 540°C.

Analysis of the corrosion product showed that under the zero oxygen/no deposit conditions a multi-layered corrosion scale formed. The outer layer was iron sulphide. Beneath this layer three other layers could be detected: each contained iron, chromium, sulphur and oxygen with the sulphur:oxygen ratio changing between the three layers. Analysis of the corrosion product under the other conditions showed that only oxide was formed, even under the deposit.

7.3 E.ON (formerly Powergen)

The higher temperatures in modern power plant have important implications with respect to fireside corrosion of materials. In supercritical units furnace walls may be operating at temperatures approaching 550ºC, and higher steam temperatures mean that the metal temperatures in superheaters and reheaters can be in the range where corrosion is severe. This project investigated the behaviour of materials under furnace wall conditions in a $1MW_{th}$ Combustion Test Facility (CTF), and under superheater/reheater conditions as components of corrosion probes installed in an operating boiler.

7.3.1 Furnace Wall Exposure Conditions

Candidate materials selected for furnace wall fireside corrosion tests were 15Mo3, T23, E911, HCM12 and 50%Cr50%Ni and 57%Cr38%Ni 2.5%Mo B Si as HVOF (High Velocity Oxy Fuel) sprayed coatings. 15Mo3 (0.3%Mo) is widely used in lower temperature furnace walls. T23 (2%Cr), E911 and HCM12 (9-11%Cr) have additions of V and W, and minor alloying elements, to improve their mechanical properties. The advantages of T23 and HCM12 are that they have high creep strength and also, in thin section, have sufficiently low hardnesses after welding not to require post weld heat treatment (PWHT). This is important in membrane wall construction where PWHT could well cause severe distortion.

Exposures were carried out in the E.ON Combustion Test Facility, which was designed to recreate real plant conditions. Six CTF runs with 12 specimens in each were conducted, each specimen making up the front face of a furnace wall probe, which was air-cooled from the back face. Three UK coals, of differing chloride contents, viz. 0.39%, 0.18% and 0.04% Cl, were used for the exposures. The furnace wall corrosion process results in aggressive linear wastage rates with negligible initiation time. As metal losses were determined using an image analysis technique that was developed in previous testwork, which had an accuracy of ±1μm [21], this meant that short-term exposures of 50 hours could be used in the tests.

After the test exposure, the corroded samples and associated corrosion scales and ash layers were examined using optical and scanning electron microscopy, together with x-ray analysis, to fully characterise the interaction between alloy, scale and ash deposits. The scale and ash deposits were characteristic of those found in actual plant.

Previous work has identified that furnace wall fireside metal losses for plain carbon steels are dependent upon metal temperature, absorbed heat flux, coal chlorine content and the oxidising/reducing potential of the local combustion environment, [21]. In particular, a synergistic effect exists between coal chlorine and heat flux, which is only active under reducing conditions. With the limited number of specimens and alloy composition as an additional variable, it was impractical to attempt a full statistical analysis of the new experimental data from the present tests. Consequently, the performance of each alloy has been evaluated with reference to the corrosion rate predicted by the findings of the previous work. This yielded a predictive equation of the form seen below, for carbon steel with metal temperatures in the range 380-450°C. The new data have been analysed to determine whether the previously determined equation holds at the higher anticipated metal temperatures and to estimate to what extent the newer alloys might be more or less corrosion resistant than plain carbon steels.

$$\text{Metal Loss} = \text{Constant} \times [(t_o \times K_{po})^{1/2} + (t_r \times K_{pr})^{1/2}] + [t_r \times ACR / 10^3]$$

Where o & r = subscripts relating to oxidising and reducing conditions

t = Time (hours)

K_p = Parabolic Rate Constant (cm^2s^{-1})

ACR = Additional Linear Corrosion Rate (nmh^{-1})

The Additional Linear Corrosion Rate is given by the following equation:

$$ACR = [(N \times Cl) \times HF^n \times \exp-(Q_{Cl}/RT)]-113$$

Where Cl = Percentage Coal Chlorine Content; N = Constant

HF = Transmitted Heat Flux (KWm^{-2}) Q_{Cl} = Activation Energy ($KJmol^{-1}$)

The measured metal losses for the 15Mo3 samples, which would be expected to have the same corrosion resistance as the carbon steels used to derive the above fit, indicate that within limits the predictive fit can be extrapolated to higher temperatures. The data suggest a peak in wastage rates at a temperature dependant upon the chlorine content of the coal fired, above which chlorine plays no further part in the corrosion process and the wastage rates are similar to that expected for a very low chlorine content coal. This is consistent with the breakdown of the aggressive chloride rich phase often found at the metal-corrosion scale interface, whose stability is limited by the partial pressure of chlorine in the combustion environment. Similar peaks in wastage rates at the same temperatures were observed for the remaining alloys and HVOF coatings.

Experience gained from plant employing alloy tubing to combat excessive corrosion would suggest that a 9% chromium addition would not provide any reduction in wastage compared with carbon steel tubing. However, the short term testing program revealed increasing chromium content in the alloy steels to improve corrosion resistance. Under oxidising conditions a logarithmic type reduction in wastage occurred resulting in a substantial reduction in losses with even the lowest chromium addition. Under reducing conditions, the addition of chromium yielded an approximately linear reduction of wastage with increasing chromium content. The equations for the calculation of parabolic rate constants were therefore amended to account for, as far as possible, the effect of chromium content under both oxidising and reducing conditions. The predicted vs. actual metal loss using these modified equations is shown in Figure 36. The data still show considerable scatter but the linear trend line fitted to the data has a slope of approximately one and an intercept close to zero.

It is unclear as to whether the benefit of chromium seen in the present short-term exposures would be seen in long-term exposures in actual plant. However the retention of major alloying elements such as tungsten within the inner corrosion scales possibly suggests that this element may be beneficial in terms of corrosion resistance.

The data for the HVOF coated samples showed considerable scatter, with the coatings often exhibiting much greater corrosion resistance than carbon steels under similar conditions. However, some coated samples showed unexpectedly poor performance, which was most probably exacerbated by their relatively defective nature, reinforcing the view that quality control is crucially important when applying coatings in order to realise their benefits.

7.3.2 Superheater/Reheater Exposure Conditions

It was determined in a previous EPRI programme that the corrosion mechanism under superheater/reheater conditions does not become established until after an initiation period of around 2,000 hours. Consequently it was not appropriate to use the CTF to simulate these environments, and corrosion testwork under these conditions was therefore conducted using probes inserted into the gas passes of a 500MW pf fired station.

Eight alloys were selected for testing in this trial, viz. (in order of increasing chromium content) Super304H, TP 347H, TP 347HFG, SAVE 25, HR3C, Sanicro 28, HR11N, IN 671. These were exposed as ring samples exposed on a support tube to form the body of a probe. Three probes in total were manufactured, each equipped with 19 separate specimens, the specimens being cooled by internal flowing air and the temperature of each specimen monitored. The probes were inserted into Unit 1 of Ratcliffe-on-Soar Power Station, two exposed local to the final reheater stage, with the third positioned behind the platen superheater stage. Exposure conditions are summarised in Table 34.

After testing, visual examination was followed by examination and analysis of the ash/slag deposits on each specimen, and detailed metallography of the surface attack. As with the furnace wall probe samples, post test metal losses were measured using an image analysis technique, this time as previously developed under an EPRI fully funded programme [22]. Metal loss and depth of internal attack were measured, and added to give a total metal wastage, which was converted to a wastage rate. It was noted that the kinetics for the development of the internal attack front almost exactly mirrored that of the total metal loss, albeit at very much lower rates.

The influence of tube metal temperature on molten salt corrosion was characterised by classic work in the late 1950s and early 1960s [23]. At relatively low temperatures (<550°C), the alumino-silicate ash deposits in contact with the tube surface and/or corrosion scale are present as a porous, solid layer. As the tube metal temperature increases, sodium and potassium sulphates, formed earlier in the furnace section, accumulate on the surfaces by condensation at the base of the porous alumino silicate deposit. As the metal temperature increases further, through the melting range of the deposit, the chemical activity of the melt increases, accelerating the rate of corrosive attack. With further increases in temperature, the stability of the alkali iron metal trisulphate corrosion products decreases until, eventually, a temperature is reached at which the rate of attack falls back to that which would be expected for corrosion solely under the influence of gaseous attack. This gives rise to the classic 'bell-shaped' curve for the rate of superheater/reheater corrosion as a function of metal temperature. The temperature range in which the molten salts are stable depends upon the interaction of the corrodent with the metal surface and its resultant corrosion products.

Evidence for a 'bell-shaped' curve for wastage rates was only suggested for the TP347H and TP347HFG steels in the present tests, with a peak in rates occurring at approximately 670°C. However, no suggestion of a bell shaped curve was seen for the Super304H material, whose corrosion rates increased steadily up to the maximum exposure temperature of 694°C, or for any of the other more highly alloyed materials.

The 300 series stainless steels were, in general, seen to be the least corrosion resistant of the alloys. Of these, the Super304H alloy showed the highest corrosion rates. Over most of temperature range on Probe C, TP347HFG suffered only half to 2/3 of the wastage of Super304H. Given that the chromium content of all three of the 300 series steels were similar, at around 18%, some other factor would appear to be responsible for this poor corrosion performance. EPRI have reported that copper is probably detrimental to the corrosion performance of superheater alloys [24], and the Super304H alloy in this study contained approximately 3% Cu. Further, localised concentrations of copper were found in the inner corrosion scales on the S304H samples in this study. Hence, it is likely that the copper content of this alloy was implicated in the poor corrosion performance.

The SAVE25 steel, containing around 23% Cr, showed corrosion rates intermediate between those of the 300 series steels and the more highly alloyed HR3C and HR11N steels. These latter steels, when exposed to the highest gas temperatures on Probe C, suffered much less corrosion damage than the Super304H and TP347HFG, exposed under similar conditions. The calculated rates for HR3C were approximately one eighth of those of Super304H and one fifth of those of TP347HFG. The HR11N sample exposed at 622°C offered the best corrosion resistance, being approximately 16 times better than the Super304H and 9 times better than the TP347HFG.

Of the specimens exposed at the lower gas temperature, IN671 performed relatively poorly. This may have been attributable to segregation in the alloy, leading to chromium-depleted regions, relative to the average alloy composition.

Overall, it is clear that in the present tests the average measured corrosion rates declined rapidly with increasing chromium content (Figure 37) and increased rapidly with increasing flue gas temperature. If 20 nmh^{-1} is taken as a tolerable corrosion rate, then, for the alloys tested and coals used during the exposures, it can be seen that only the high alloy materials HR3C, HR11N and IN671 possessed sufficient corrosion resistance under all conditions examined to meet this criterion.

Under the relatively low gas temperatures to which the TP347H and SAVE25 materials were exposed, these materials would also have sufficient corrosion resistance to meet the design criterion. However, no samples of these materials were exposed at the highest gas temperatures and it is uncertain as to their ability to meet the criterion under these conditions.

The 300 series alloys Super304H and TP347HFG both exhibited metal wastage rates in excess of the design criterion at high metal temperatures, particularly where high gas temperatures also occurred. Hence, these alloys would not be suitable for use in the highest heat flux areas. However they may find application within the primary superheater and reheater, where metal and gas temperatures are relatively low.

7.4 Mitsui Babcock

For onerous environments, which include the higher temperature ranges in which furnace wall tubes and superheater/reheater tubes in coal fired stations are being asked to perform, one alternative to the use of highly alloyed monolithic materials is the employment of sprayed metallic coatings. Aspects of corrosion resistance of such coatings have been fairly widely investigated within the Plant Integration Group of COST 522, but mainly in the context of the lower temperature but extremely aggressive environments arising in waste incineration and biomass firing. However, sprayed metallic coatings may also have a part to play in coal fired stations, certainly in areas subject to more severe corrosion such as leading tubes in superheaters and reheaters.

A limited number of specimens were exposed in the CTF in the work done by E.ON under 7.3.1 above, which concluded that a crucial aspect with respect to the corrosion resistance is the quality of the application. To complement this, the work performed by Mitsui Babcock mainly concerned the integrity of coatings and their substrate adhesion under creep and thermal cycling conditions.

Two substrate materials were employed, viz. 2¼%Cr 1%Mo and TP 316 stainless steel, as being representative of commonly used ferritic and austenitic steels, and thereby providing two different coefficients of thermal expansion. Different forms of these materials were obtained for the three types of test; tubing for thermal cycling experiments (performed on TP 316 tubes only), bar for creep specimens and plate for corrosion coupons.

It was decided to employ High Velocity Oxy Fuel (HVOF) spraying as the coating method as it is used quite widely and generally provides a satisfactory product. Discussions were held with the University of Tampere (Finland), one of the COST 522 partners in the Corrosion Group, and also expert in the field of metal spraying and testing, to determine which coatings were likely to have the best attributes for the uses envisaged. Remembering that two substrates are involved in the creep testing, in order not to generate too large a testing matrix, two coating types and two coating methods were identified, and put together into three combinations as follows:

i) Ni - 50%Cr, sprayed using the High Velocity Oxy-Fuel (HVOF) process, by the University of Tampere (identified in subsequent text as Ni-50Cr)

ii) Ni - 56%Cr 2.5%Mo + Si + B, sprayed using the HVOF process by University of Tampere (identified in subsequent text as SX)

iii) Ni - 50%Cr, sprayed using a commercial contractor and the HVOF process, (identified in subsequent text as COM).

Thermal cycling tests were conducted only on the Ni-50Cr and SX externally coated tubes, as the commercially produced coatings did not arrive in time for them to be included. The substrate used was TP 316 stainless steel as the upper temperature employed was 650ºC. The tube was heated in an infrared 'clam shell' furnace to 650ºC at the centre position, and then cooled in flowing air to below 100ºC. An extract from the logging record is shown in Figure 38. Whilst the cooling part of the cycle is not rapid enough to constitute a thermal shock where, e.g. ceramic materials are concerned, it is severe for a boiler tube, where such a temperature change may normally take a number of hours.

After 1000 of these cycles, the specimen was demounted, examined visually and by dye penetrant for any cracking or fissures, and then sections were taken for metallography. Only mild discolouration of the specimens was seen, with no evidence of the development of coating defects or cracking.

All three coating variants were applied to creep specimens manufactured from both the 2¼%Cr 1%Mo and TP 316 substrates. After coating, gold spot markers were deposited at 1mm intervals on the gauge lengths of a number of the coated specimens, and base measurements made to ± 2µm between the centres of these spots using a Zeiss Universal Measuring Microscope. Specimen diameters at 3 positions around the circumference were also measured. After measurement, the specimens were tested in creep for durations between 1300 and 3700 hours. It was the intention to try to stop the tests when sufficient strain had accumulated to have a good chance of producing defects in the coating, but before final failure, however this was not always successful. Nevertheless, all specimens equipped with gold spot markers were remeasured and local strains calculated, along with reductions in area from the remeasured diameters. Diameters only were measured and area reductions calculated from specimens without spot markers.

Figure 39 shows defects found in a Ni-50%Cr HVOF coating after test, and Figure 40 a specimen with gold spot markers after test and the co-incidence of high local strain and defects. The complete set of results from the creep tests is given in Table 35, which indicates that to cause defects in any of the coatings tested would require greater than around 12.5 % strain, and in the case of the Ni-50%Cr coatings maybe even more than 20%. These are high values, and it is concluded that during the normal lifetime of a tube, whether it be ferritic or austenitic, the creep of such tubes would not cause any distress to any of the applied HVOF coatings tested.

A limited number of simple corrosion tests were conducted to see if the coatings could be ranked in order of resistance without reverting to complex atmosphere testing. Conditions used were tests in air with a synthetic superheater deposit of $K_2SO_4/Na_2SO_4/Fe_2O_3$ in the molecular ratios of 1.5/1.5/1.0, and tests in argon with a synthetic furnace wall deposit of 60% FeS and 40% Fe_3O_4 . Coating thicknesses were measured microscopically on the polished sides of the corrosion coupons before test, and on a section through the centre of the coupon after test. It was noted that whilst the coatings applied by the University of Tampere were consistent in thickness and close to the 300 μm target, the commercially applied coatings were far more variable.

No significant change was seen in the coating thicknesses before and after testing, (1000 hours at 570-750ºC for superheater conditions and 500-600ºC for furnace wall conditions). Although some corrosion penetration of the coating was seen at the highest exposure temperatures, and subjectively there may appear to have been less corrosion on the Ni-50%Cr in the superheater conditions, this was not really borne out by the measurements, as the standard deviations were large. Consequently it was not possible to definitively rank the coatings using these tests.

8. CONCLUSIONS

8.1 General

With 15 partners from the UK, the contribution to the COST programme from this source has been both large and extremely valuable. In the quest for stronger and more oxidation resistant alloys, it is clear that the task of developing and validating a new alloy is extremely onerous and expensive for a single organisation. Even with such tools as neural networks etc., the evaluation of any findings requires a systematic approach to the effect of alloying elements and factorial experiments involving many casts of material to be tested. When such evaluations involve extended creep testing at a number of temperatures, the logistics, work content and cost are enormous. In practical terms often the only way to do this in a methodical rather than piecemeal way is to share the work and cost with a number of collaborating partners. As well as sharing the cost, these partners can bring to bear their own particular expertise towards a common goal.

This is where an organisation such as COST proves its worth, not only as an umbrella organisation which provides an overview of and directionality to the work programme, but also as a referee to ensure that each contribution from an individual partner is useful and meaningful, fitting into the overall scheme of development.

Thus in this case the endorsement of the individual programme(s) by the COST committee is also an assurance to any national organisation, which may be approached for grant funding, that such funding will be spent in an appropriate and useful manner, and that value for money will be achieved. In the UK this national organisation is the Department of Trade and Industry (DTI), who provided support in the form of grant aid to the UK partners.

Obviously, in a collaborative programme, success is dependent on information and data sharing, the aim in the present case being to gain advantage for European technology and manufacturing in the global market. National programmes of process and plant development have been put in place in Japan and the USA, and it was considered vital that the European power industry was also involved in advanced plant development. To this end, the amount of effort expended in the UK in COST 522 corresponds to around £2,400,000, and when the work, results, correlation and analysis from other European partners is added in, the total expenditure in the COST 522 project is in the region of 25 – 30 million Euro. As well as the overall European goal, there are obviously more parochial advantages to be gained for the individual UK companies involved, such as expansion of data bases, knowledge acquisition to aid marketing efforts, 'hands on' experience of new materials and process methods such as welding and fabrication, etc.

8.2 Technical

The overall technical conclusions arising from the various sections of the UK programme are detailed below:

Boiler Group

The COST 501 boiler materials programme was focussed primarily on testing and qualification of the thick walled pipe material E911, and this material is now in operation at temperatures up to 600ºC. In the COST 522 programme, target temperatures were raised by a further 25 – 50K, and the critical boiler components which must be upgraded to cope with the increase in steam parameters were identified as the furnace walls, the last stages of the superheater and reheater heating surfaces and the thick walled components such as headers and pipework.

For furnace walls, the major effort was concentrated on the validation of T/P23 material for higher application temperatures. In this work, there appeared to be little effect of wall thickness on tensile properties. A membrane panel assembly in T23 tubing including a ninety-degree bend was successfully fabricated. It was confirmed that satisfactory hardnesses were obtained without the application of either preheat or post weld heat treatment. Satisfactory weld procedure qualification tests were developed.

Chemical compositions of 11-12%Cr steels have been proposed based upon the results of oxidation and mechanical tests of other steels in this group, and on predictions from alloy design tools. Several small melts have been produced by V & M and Corus, all with at least 11%Cr to promote oxidation resistance. The longest creep and thermal exposure tests have reached more than 15,000 hours, and the most promising melts are showing creep rupture strengths similar to P92 but greatly enhanced oxidation resistance, thereby satisfying the targets of the project.

Four new austenitic steels based on Esshete 1250 but with increased Cr content have been manufactured by Corus. The most promising of these has shown creep properties similar to Nf 709 for temperatures up to 650ºC and above, for times greater than 5,000 hours to date, and enhanced oxidation resistance over the original Esshete 1250 material. Hence similar oxidation resistance to Nf 709 has been achieved at lower cost, and the ongoing creep tests are looking promising and will permit an overall evaluation to be made.

Development work at Metrode looked at consumables for P92, T23, E911 and P122 materials and all commonly used welding processes (solid wires for gas tungsten arc welding (GTAW), submerged arc welding (SAW), covered electrodes for shielded metal arc welding (SMAW) and tubular wires for flux cored arc welding (FCAW). The work has led to commercial availability of GTAW and SAW wires and a SMAW electrode for P92, and a SMAW electrode for T23. Further development/testing of FCAW electrodes for P92 and T23 is continuing.

Despite low absorbed energy and small CTOD values, assessment of a P91 FCAW weldment in the post weld heat treated condition has predicted a large critical flaw size, easily detectable by common NDT methods. The results support the view that current code requirements may be pessimistic and onerous in relation to fitness-for-purpose criteria.

A group of SMAW electrodes was produced to provide a matrix of systematically varied compositions in four groups, with Cr varying within each group between 8.5% and 12%. Mo, Co, Cu and W were also varied. The best correlation between weld metal Cr equivalent and delta ferrite content was found by using the coefficients proposed by Ryu and Yu. The detrimental effect of ferrite on weld metal impact toughness was also demonstrated quantitatively. These relationships would indicate that Cr equivalent should be controlled to a level of <9-9.5% to minimise the ferrite content.

E.ON UK (formerly Powergen) have investigated the potential implications of low weld metal creep ductility for plant integrity, in order to develop better consumables for advanced plant. P91 parent material and MMA and FCAW weld metals were employed as model materials for more advanced steel compositions. Strain monitored creep tests to failure were carried out on parent material and weld metals covering a range of short term test conditions at varying temperatures and stresses. The data on rupture life, creep ductility, and strain accumulation during primary, secondary and tertiary creep were analysed. It was shown that different factors governed these different stages of creep. Low weld metal secondary creep ductility was shown to be of some concern, and appeared to be inversely correlated with creep strength. Hence, weld metals should be developed for optimised creep ductility with adequate but not excessive long term creep strength.

Interrupted testing was undertaken to clarify how creep damage development is related to the creep strain curve. It was found that while microstructural degradation is the dominant factor determining the shapes of creep curves in parent material, creep damage and cracking occur at an earlier stage of creep life in weld metals, and are partly or wholly responsible for their reduced ductilities. Further work will be needed to understand why weld metals differ from parent materials in this respect, and what can be done to develop improved weld metals with higher creep ductility.

Turbine Group

Two COST steels have been qualified for rotors in steam turbines, and a COST steel and a steel developed in an EPRI programme for casings and valve chests, for steam temperatures up to 600ºC. A boron containing steel appears appropriate for rotors in steam turbines up to steam temperatures of 620ºC.

Based on commercial tools such as ThermoCalc and Dictra, phase stability calculations and considerations of parameters such as transformation temperatures, a series of new compositions was drawn up. These were produced as cast and forged trial melts and an extended test programme has been performed. Potential candidate materials for steam temperatures of 620ºC (and possibly 630ºC) have been identified.

The concept followed for even higher temperatures, up to 650ºC, viz. increasing the chromium content and compensating for delta ferrite by significant cobalt levels, has failed. All trial melts produced according to this concept could not reach the creep strength of the boron alloyed heats. The latter still exhibit the highest and most stable creep behaviour, and reliable data are available up to 100,000 hours. The experience in manufacturing high boron containing large melts has been significantly increased since the early COST work, and further work is likely to be focussed on this alloy concept. A series of boron alloyed steels without elements like tungsten and cobalt has been defined and produced in the form of trial forged and cast melts. The evaluation of these melts has recently been started.

The improved creep strength of the new ferritic steels does not enable them to substitute for nickel alloys in bolting applications.

Welding

The major input into this group from the UK was concerned with weld filler materials.

ESAB conducted a statistically designed experiment with 24 specially produced wires in which Cr, Mo, Co, W, Ti and B were varied. Alloying with Ti and B both increased the weld metal yield stress but reduced its toughness. Chromium did not strengthen, but reduced toughness, whereas Mo, W and Co had no discernable effect. Toughness could be increased with increasing PWHT temperature (730 to 760ºC), or the time at temperature, both of which also caused softening.

TWI again looked at achieving a good balance between toughness and creep strength, using two tungsten containing steel grades, one with 9%Cr and the other with 11%Cr. Although the welds containing changes to the Ni and Co content showed a large improvement in creep strength, this was at the expense of creep ductility, which was best in the base compositions.

Microstructural modelling has links with both the boiler group activities and with the welding group. Loughborough University have been modelling the formation of delta ferrite in weld metals in terms of Cr* and Ni* equivalents, using the programme MTDATA. A procedure was developed to estimate the efficiency of alloying elements to promote either delta ferrite or austenite. Experimental data on delta ferrite in the weld zone were treated in terms of Cr* and Ni*. Wagner’s theory of diffusion phase growth was used to analyse the process of delta-ferrite decomposition in the centre bead of weld metal. Modification of Wagner's theory allowed the description of delta ferrite content as a function of steel composition. It was shown that Cu accelerated the process of delta-ferrite decomposition, rather than Co and Ni, and hence steels doped with Cu could have a higher concentration of Cr that would allow an improvement in service properties such as resistance to oxidation.

Metallography and Alloy Design

The prime motive of the activities in COST 522 (and before that in COST 501) has been a greater understanding of microstructural behaviour to enable better alloy design. The consensus view on key aspects for design of high temperature 9-12%Cr martensitic alloys has been reinforced, and is summarised below:

Factors necessary for high creep strength:

- Fully martensitic microstructure
- A dispersion of M23C6 carbides to stabilise sub-grain boundaries
- A dispersion of MX particles to inhibit dislocation movement within sub-grains
- Additions of boron to stabilise the carbide structure

Factors necessary to avoid degradation of properties during long term service

- Freedom from precipitation of Z-phase, M_6C and M_2C, achieved either through design of the thermodynamic equilibrium to ensure such phases are not present or through designing the steels so that these phases are kinetically inhibited over the lifetime of the power plant.

A further benefit from the work has been the creation of a source against which the in-service evolution of power plant component microstructures can be assessed to assist in the life assessment of plant using 9-12%Cr steels.

Oxidation and Protective Systems

Alstom provided industrial steering to the activities of the Oxidation and Protective Systems group, which involved a number of partners in continental Europe. NPL also contributed to this group, and their investigations are summarised under the Plant Integration Group below.

The conclusions from the Oxidation Group itself are as follows:

1. There was fairly good agreement between the results from the different participating laboratories in short-term exposures in steam. The tendency for spalling led to somewhat larger scatter of the data after longer exposure times.
2. Chromium and silicon have a major influence on the kinetics of oxidation. Chromium contents greater than 11% and silicon contents greater than 0.3% lead to significant reductions in the rate of oxide growth.
3. Unresolved issues concern the effect of steam pressure and the tendency of the oxide scales formed in steam to spall.

4. There is promising potential for the application of coatings to enhance the steam oxidation resistance of Cr steels. Further development is required to optimise the processes for large components and to investigate the effects of the coating on mechanical properties.

Plant Integration Group

A number of projects were conducted under the auspices of this group, all directly or indirectly concerned with corrosion.

For laboratory tests under co-firing conditions at Cranfield on specimens with KCl/K_2SO_4/pf ash deposits, results showed that there was increasing levels of corrosion damage with decreasing alloy chromium content, increasing temperature, increasing levels of K_2SO_4 + KCl in the deposit, and higher ratios of KCl/K_2SO_4.

Coal and biomass co-firing was performed in the 150kW combustion test facility at the Power Generation Technology Centre at Cranfield University, with the following fuel mixes : coal with normal operation, coal-20% straw and coal-20% wood. Tests were performed for 50-100 hours. Results indicated that the levels of damage anticipated for dilute mixes of biomass in coal were similar to the ranges of damage observed for coal or wood firing alone.

NPL carried out steam oxidation testing in flowing steam in a laboratory test rig, and developed a model to predict the onset of scale cracking and spalling. Rules were developed for the evolution of the individual layers within the scale with time, and using these, model predictions were made of the temperature drop to initiate cracking and spallation of the magnetite as a function of total scale thickness. It was found that the model represented an adequate description of this limited dataset, although further refinements to the model are likely to improve the overall fit.

In addition, NPL investigated metal wastage rates of the furnace wall materials T22 and T23 under simulated low NOx combustion atmospheres at 440 and 540°C. The work showed several systematic trends as the temperature, gas composition and deposit were varied. In the absence of both oxygen and a FeS/Fe_3O_4 deposit the metal loss kinetics are linear whereas if oxygen, deposit or both are present the metal loss kinetics are parabolic.

E.ON (formerly Powergen) conducted corrosion testing in simulated furnace wall corrosion environments in a $1MW_{th}$ pulverised coal Combustion Test Facility. The performance of each alloy was evaluated with reference to the corrosion rate equation predicted by the findings of previous work, but at higher anticipated metal temperatures. Under oxidising conditions a logarithmic type reduction in wastage occurred, in comparison with carbon steel, with even the lowest chromium addition. Under reducing conditions, the addition of chromium yielded an approximately linear reduction of wastage with increasing chromium content. The equations for the calculation of parabolic rate constants were therefore amended to account for, as far as possible, the effect of chromium content under both oxidising and reducing conditions. The predicted vs. actual metal loss using these modified equations still show considerable scatter but the linear trend line fitted to the data had a slope of approximately one and an intercept close to zero.

Long term tests were carried out using air cooled corrosion probes in three superheater/reheater locations in an operating utility boiler, for times between 8000 and more than 10,000 hours, followed by measurement and analysis of results. Evidence for a 'bell-shaped' curve for wastage rates was only suggested for the TP347H and TP347HFG steels in the present tests, with a peak in rates occurring at approximately 670°C. However, no suggestion of a bell shaped curve was seen for the Super304H material, whose corrosion rates increased steadily up to the maximum exposure temperature of 694°C, or for any of the other more highly alloyed materials.

The 300 series stainless steels were, in general, seen to be the least corrosion resistant of the alloys tested. The SAVE25 steel, containing around 23% Cr, showed corrosion rates intermediate between those of the 300 series steels and the more highly alloyed HR3C and HR11N steels. Overall, it is clear that in the present tests the average measured corrosion rates declined rapidly with increasing chromium content and increased rapidly with increasing flue gas temperature.

Mitsui Babcock looked at the integrity of HVOF coatings under creep and thermal cycling conditions, and also performed some simple air atmosphere tests on coated coupons covered with synthetic deposit, for comparison with the simulated atmosphere tests performed by other partners. None of the coatings showed any signs of distress after the thermal cycling (1000 cycles from 650ºC down to <100ºC and return, 1 cycle taking around 15 minutes). Creep tests, using gold spot markers to monitor local strains, indicated that the levels of strain to cause the appearance of coating defects was approximately 12.5% or above for all coatings. It was concluded that during the normal lifetime of a tube, whether it be ferritic or austenitic, the creep of such tubes would not cause any distress to any of the applied HVOF coatings tested.

The corrosion tests with synthetic deposits caused some amount of corrosion on the specimens exposed at high temperatures, but the scatter in the results, giving very large standard deviations, meant that no definitive conclusions could be drawn on this aspect.

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11. ABBREVIATIONS USED IN TEXT

AE	Acoustic emission
ASME	American Society of Mechanical Engineers
AWS	All weld specimen
CTF	Combustion Test Facility (E.ON UK)
CTOD	Crack Tip Opening Displacement
DTI	Department of Trade and Industry (UK)
EFTEM	Energy Filtered Transmission Electron Microscopy
EPRI	Electric Power Research Institute (USA)
FBC	Fluidised Bed Combustor
FCAW	Flux Cored Arc Welding
FEA	Finite Element Analysis
GTAW	Gas Tungsten Arc Welding
HAZ	Heat Affected Zone
HVOF	High Velocity Oxy Fuel
LMP	Larson-Miller Parameter
MMA	Manual Metal Arc
PF	Pulverised Fuel
PWHT	Post weld Heat Treatment
SAW	Submerged Arc Welding
SIMS	Secondary Ion Mass Spectrometry
SMAW	Shielded Metal Arc Welding (same as MMA above)