dti

ADVANCED PF POWER PLANT

Improved Materials for Boilers and Steam Turbines

PROJECT SUMMARY 292

CLEANER FOSSIL FUELS PROGRAMME
– CLEANER COAL R&D PROGRAMME

OBJECTIVES

The principal aim of this project was to develop and demonstrate the suitability of advanced materials and components for the power industry. Such materials and components were aimed at steam temperatures of 620 - 650°C. Specific areas covered were:

- Development and assessment of improved alloys for boiler superheaters, headers, pipework and furnace walls.
- Development of improved alloys for steam turbine high temperature rotor forgings, castings, and bolting. Prototype component manufacture and characterisation.
- Development and modelling of welding procedures and consumables for the above groups.
- Accelerated alloy development and application through improved understanding and modelling of microstructural evolution and its relationship to mechanical properties.
- Characterisation of steam oxidation behaviour of new alloys, and modelling of spallation.

SUMMARY

Boilers: Consideration of factors concerned with microstructure and strength has led to the production of a number of martensitic and austenitic development alloys and subsequent evaluation for the selection of the best alloy from each group. Testing of these is ongoing. The implications of low weld metal ductility for plant integrity have been investigated and the relationship between creep

Figure 1. Changshu Power Station; 3 x 600 MW supercritical units under construction (courtesy of Mitsui Babock)

damage development and the creep curve has been clarified.

Welding: Selected elements in welding consumables have been systematically varied in a number of experiments. The effect of these on toughness and strength has been examined, together with the effect of post weld heat treatment. The formation of delta ferrite in weldments and how it is influenced by composition has been studied and modelled. A recommendation for a maximum chromium equivalent (Creq) to minimise delta ferrite has been made.

Steam Turbines: Long term programmes on forgings and castings are ongoing, with alloy variations being systematically tested in creep tests with aims of more than 100,000 hours. New trial melts with the potential of operation up to 650°C have been assessed in the current programme and are also undergoing creep testing which is being continued under DTI Project 409 (see Project Profile 367 URN 05/964). Testing of both ferritic and nickel based candidate alloys for high temperature bolting has taken place and is continuing.

Metallography and Alloy Design: Neural network analysis, using a large compositional database, was employed to predict creep rupture life of austenitic stainless steels. The findings were verified on an advanced austenitic steel NF 709.

Oxidation: A model of scale failure by cracking/spallation has been developed, and the results of steam oxidation tests used to validate the model.

Corrosion and Life Prediction: The behaviour of materials under furnace wall conditions was determined both in laboratory tests and in a 1MW Combustion Test Facility. Superheater corrosion was investigated by exposing multispecimen cooled probes in an operating utility boiler. The effect of biomass co-firing with coal was investigated both in laboratory tests and in a combustion pilot plant modified to handle biomass fuels.

BACKGROUND

The Foresight Task Force highlighted that the economic and environmental performance of Advanced PF technology was currently limited by the performance of high temperature materials for boilers and steam turbines and outlined the required Research & Development programmes perceived as being necessary for the development of improved materials. The UK power generation industry responded to these 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 620-650°C, 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.

EXPERIMENTAL WORK

Mechanical properties of three experimental martensitic alloys were determined, including short and long term stress rupture results. A similar exercise was carried out on experimental austenitic alloys based on the high manganese Esshete 1250 alloy. Welding development, including mechanical and Charpy impact tests, was carried out on the following experimental consumable types, all 9-12%Cr except where shown.

- T23 type Manual Metal Arc (MMA) with different Ni and C.
- T23 type Flux Cored Arc Welded (FCAW) with different Ni and higher C, Nb and B.
- P92 type Tungsten Inert Gas (TIG), MMA and FCAW (similar composition to P92 with more Mn allowed and some Ni added).
- E911 & P122 type FCAW.
- MMA electrodes in four groups, Cr-Mo, Cr-Mo-Co, Cr-Mo-Cu and Cr -W-Cu, each group with four Cr contents.
- A statistically designed experiment used 24 experimental consumables with variations of Cr, Mo, Co, W, Ti, and B.
- Variants on the current (commercial) Manual Metal Arc electrodes for NF616 and HCM12A W containing steels, in terms of Ni and Co contents.

Microstructural modelling was carried out on the formation of delta ferrite in alloys containing 8 - 12% Cr.

The implications for plant integrity of low weld metal ductility have been investigated by examining the relationship between creep damage development and the creep curve.

Seven trial melts for steam turbine forgings were made and extensively tested (metallography, tensile and impact tests, fatigue crack growth and creep testing). Further work has been started on new steels with higher boron contents. Development of casting steels has been similar to that for forgings, with six trial melts still undergoing creep testing. Results have led to new compositions similar to those for the latest forging materials, and long term tests have been initiated. Stress rupture testing and stress relaxation testing is still ongoing for the martensitic bolting alloys; some testwork on the nickel based alloy has been completed.

Fireside corrosion was measured in both a laboratory test (furnace wall low NO_X simulation), a combustion test rig (furnace wall simulation, with different Cl coals) and on probes inserted into a power station superheater region. The test rig results were compared with a model equation derived from earlier work. Laboratory tests with synthetic deposits, and exposures in a combustion test facility were used to follow the progress of corrosion in coal/biomass co-firing. A steamside oxide spallation model has been tested on P92 specimens oxidised in flowing steam.

RESULTS

From the experimental alloys both in 9-12%Cr steels and austenitic steels, a best candidate from each group has been selected and longer term creep tests have been initiated. The martensitic steel has similar short term creep properties to P92 but superior oxidation resistance. The creep tests will be continued under DTI project No. 409 to determine long term behaviour. A group of 16 MMA 9 - 12%Cr type electrodes, with variations in Cu, Co, Mo and W, were used to evaluate the best of the proposed relationships of Cr equivalent with alloying elements, and the ensuing Creq with weld delta ferrite content. Based on the Ryu and Yu coefficients, the Creq to minimise ferrite content should not exceed 9 - 9.5%. This was found to be consistent with a Charpy energy above 30J at 20ºC. The same alloy groups were used in the modelling of the formation of delta ferrite-austenite mixtures in weld metals in terms of Creq and Nieq. It was shown that Cu accelerated the process of delta-ferrite decomposition, hence steels with higher Cu contents could have a higher concentration of Cr, which would allow an improvement in service properties such as oxidation resistance.

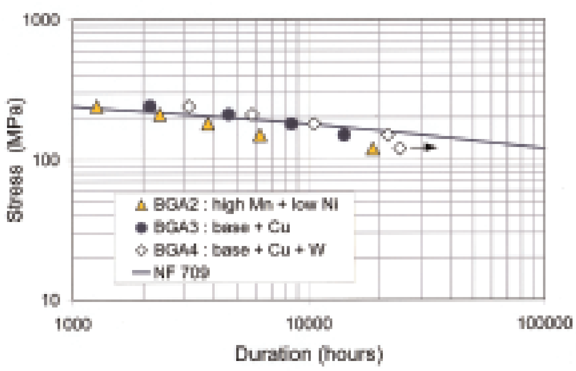

Figure 2. Creep tests on experimental austenitic alloys (Graph courtesy of Corus UK)

In the programme using 9 - 12%Cr type consumables with variations in Cr, Mo, Co, W, Ti and B, regression analysis on wire composition indicated adverse effects of Cr, Ti and B on toughness. Running the analysis with proof stress included dropped Ti out of the equation. The programme on 9-12%Cr welds with variations in Ni and Co indicated that 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.

Creep rupture data from P91 parent, MMA and FCAW weld metals were obtained and analysed in a number of ways.

It was tentatively concluded that a Monkman-Grant type parameter was the best practical measure of the relative secondary creep ductility of the weld metals. Interrupted creep tests indicated that damage was only generally detectable at a strain level typically corresponding to over 90% life fraction.

Both experimental melts and full size components have been manufactured and tested during the turbine castings and forgings programmes. After 15,000 hours creep testing on seven trial melts for rotor forgings, it was noted that none of the new melts offered a clear improved behaviour over the best of previous melts. However, the melts with higher Cr have better oxidation resistance and are still better than the 600ºC materials with W and Mo, so testing is continuing with these. It was decided that future work will be focussed on B containing steels, and new steels have been designed with contents of Cr, B and N systematically varied (B at 100 - 300 ppm). These have been manufactured and are under test at present.
Development of new casting steels has followed quite closely that for forgings, with creep tests to 20,000 hours on the last batch of melts indicating no clear advantage over previous compositions. New melts with B in the range 100 - 300 ppm and no Co or W additions have been manufactured and are under test.

Using alloy X19CrMoNbVN11.1 as a base composition for bolting alloys, variations with increased N are under test as plain and notched bar specimens, and so far reveal that the lower N variant is giving longer plain rupture lives, with no clear effect on notched rupture. Stress relaxation tests have reached around 10,000 hours of a targeted 30,000 hour test life. In the nickel alloy tests, it has been demonstrated that the INCONEL® alloy 783, tested as 54 mm diameter bar, and full scale bolts from the bar, will be suitable for bolting, and procurement of 100 mm diameter material is being instigated for further confirmatory tests.

Analysis of data from laboratory tests on T22 and T23 simulating furnace wall conditions indicated the effect of oxygen content and deposit on metal wastage. If oxygen, deposit, or both were present the metal loss kinetics were found to be parabolic rather than linear. The combustion test facility exposures used a number of different materials. Benefits were seen for higher Cr contents, but it was unclear whether this benefit would be maintained in long term exposures in plant. However the retention of W within the inner corrosion scales may suggest that this element may be beneficial. The superheater probe exposures, which were much longer term (8,129 to 10,927 hours), showed clearly that the average measured corrosion rates decreased rapidly with increasing Cr content.

The laboratory tests simulating biomass co-firing showed that there was increasing levels of corrosion damage with decreasing Cr content in the alloys, increasing temperature, increasing levels of K_2SO4 + KCl in the deposit, and higher ratios of KCl/K_2SO4. In the combustion test facility, using coal under normal and low NO_X conditions, and with 20% straw or 20% wood, the deposit compositions from co-firing were not significantly different from those with coal alone, and this was found to carry through to the material performance. This was not expected for the straw, which however had an unexpectedly low Cl level, and this was thought to be responsible.

A model of steamside oxide spalling was formulated based on the calculation of stresses developed during cooling in each oxide layer, assigning a fracture energy to the magnetite layer, and adopting a pragmatic criterion that spallation occurred after a further 200°C temperature drop after first cracking of the magnetite. Model predictions of temperature drop required to cause spalling of the magnetite as a function of total scale thickness after oxidation showed the model to represent an adequate description of the limited dataset obtained.

CONCLUSIONS

A new ferritic and a new austenitic alloy which show promise of improved properties have been developed, and are undergoing long term creep testing which will be continued under DTI Project 409. In the programme using 9-12%Cr type welding consumables, a number of conclusions were reached:

- To minimise ferrite content, the Cr equivalent based on the Ryu and Yu coefficients should not exceed 9 - 9.5% Modelling indicated that Cu additions would be beneficial in allowing an increase in Cr content without increasing delta ferrite.
- In tests with variations in Cr, Mo, Co, W, Ti and B, the effect on toughness did not rule out any particular approaches to alloying, but there was a clear suggestion that Ti and B would be least preferred if high temperature properties could be achieved by other means.
- In MMA welds based on 9%Cr and 10.5%Cr type compositions with approximately 1.5%W, variations in Ni and Co indicated that the highest toughness after PWHT was obtained for the addition of 1%Co to the base composition.

The analysis of creep rupture data from P91 indicated that failure was principally caused by strain-induced microstructural degradation and hence accelerated creep deformation into the tertiary regime. For rotor forgings, it was concluded from initial stress rupture testing that complex and expensive alloying with Co would not fulfil the expectations with regard to creep strength. Hence, new alloys were designed with higher B contents and these are also under test at the present time. Alloys of similar composition for castings are also on test, and such tests will be ongoing in the DTI Project No. 409. Both martensitic and nickel based alloys are still under test for use as bolting materials.

Laboratory testwork under furnace wall conditions indicated that if oxygen and/or deposit were present metal loss kinetics would be parabolic. Combustion rig tests suggested benefits from Cr and W in the material, but indicated that the former may be short term. Superheater probe tests however indicated a beneficial effect of Cr on corrosion resistance under these conditions over a longer term exposure. In biomass co-firing, Cr in the alloy was beneficial whereas increased levels of K_2SO4+KCl in the deposit and higher ratios of KCl/K_2SO4 were not.

POTENTIAL FOR FUTURE DEVELOPMENT

Development is already continuing on the alloys and welding consumables developed in this programme. Long term creep testing on martensitic and austenitic alloys for superheater tubing, and 9 - 12%Cr alloys for turbine forgings and castings are ongoing. Weld procedures for the new alloys are being developed, using existing and experimental weld consumables developed in this programme. Weld procedure qualifications will be made and weldments subject to mechanical testing and long term creep rupture exposures. The final aim will be to qualify the new alloys for use at 650°C. Data are still required on the corrosion and oxidation behaviour of the new materials and welds to enable this goal to be met.

Further information on the Cleaner Fossil Fuels Programme, and copies of publications, can be obtained from:
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COST

The total cost of this project is £2,446,172 with the Department of Trade and Industry (DTI) contributing £1,187,965 The balance of funding was provided by the participants.

DURATION

63 months - September 1999 to November 2004

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