Development and Validation of Advanced Oxidation Protective Coatings for Super Critical Steam Power Generation Plants

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Abstract

Increasing the efficiency of coal-fired power plant by increasing steam temperatures and pressures brings benefits in terms of cheaper electricity and reduced emissions, particularly CO_2. In recent years the development of advanced 9%Cr ferritic steels with improved creep strength has enabled power plant operation at temperatures up to 600 - 620ºC such that these materials are currently being exploited to construct a new generation of advanced coal-fired plant. However, the move to higher temperatures and pressures creates an extremely hostile oxidising and errosive environment. To enable the full potential of the advanced 9%Cr steels to be achieved, it is vital that protective coatings are developed, validated under high pressure steam environments and applied successfully to candidate components from the high pressure steam path. This paper reviews recent work conducted within the Framework V Brite EuRam project "Coatings for Supercritical Steam Cycles" (SUPERCOAT) to develop and demonstrate advanced slurry and thermal spray coating technologies capable of providing steam oxidation protection at temperatures in excess of 620°C and up to 300 bar pressure. The programe of work described has demonstrated the feasibility of applying a number of candidate coatings to steam turbine power plant components and has generated long-term steam oxidation rate and failure data that underpin the design and application processing work packages needed to develop and establish this technology for future and retrofit plant.

Keywords: 9%Cr steels, steam oxidation, protective coatings, aluminising, thermal spraying

Introduction

Increasing the efficiency of coal-fired power plant by increasing steam temperatures and pressures brings benefits in terms of cheaper electricity and reduced green house gas emissions, particularly CO_2 [1]. As illustrated by Figure 1, over recent years a series of advanced, more creep resistant ferritic, forged and cast steels have been developed to meet the demands for high temperature, more efficient and reliable power plant that remains cost effective to manufacture and operate. These developments have been achieved through alloy design and long term testing of candidate materials that has led to a gradual reduction in the chromium content of the steels and the introduction of additions such as tungsten, vanadium, niobium and boron [2] and has culminated in the 9%Cr ferritic steels such as P91 (X12CrMoVNbN9-1) and P92 (X10CrWMoVNb9-2) and more latterly the COST steels such as FB2 (X13CrMoCoVNbNB9-2-1) and CB2. However, the reduction in chromium content has had a detrimental effect on the oxidation resistance of the steels as operating temperatures have increased [3]. These steels now offer the potential for power plant operation at temperatures up to 600 to 620ºC and are currently being exploited to construct a new generation of advanced coal-fired plant in Europe, Japan and China. Table 1 sumarises the current state-of-the-art for high performance plant operating in Europe that offer efficiency levels as high as 49%. The advent of high temperature, super critical steam turbines creates an extremely hostile oxidising and errosive environment for the components that may lead to excessive oxide scaling and loss of component profile due to exfoliation and erosion that may impact directly upon plant operation and efficiency, component durability and overhaul procedures.

To enable the full potential of the advanced 9%Cr steels to be achieved, it is vital that candidate protective coatings are developed, validated under high pressure steam environments and applied successfully to components from the steam path (main and re-heat steam pipe, steam chest & valve assemblies, turbine blades). Without these complimetary advances in coatings technologies, the problem of excessive oxidation may offset many of the potential economic, environmental and performance benefits that can be achieved. This paper briefly reviews recent work on processing and testing of selected coatings produced within the Brite EuRam FPV "Coatings for Supercritical Steam Cycles" (SUPERCOAT) project, led by ALSTOM Power in collaboration with seven partner organisations from across Europe (see Figure 2), to develop and demonstrate candidate slurry and thermal spray coating technologies that offer the capability of providing increased component reliability, extend plant life and increase performance of supercritical steam turbines operating at temperatures in excess of 620°C and up to 300 bar pressure. The programe of work described has demonstrated the feasibility of applying a number of candidate coatings to samples of P92 and steam turbine power plant components, as follows:

- Slurry aluminising (diffused aluminium paint)
- High velocity oxy-fuel (HVOF) deposition of metallic and Cermet powders (Ni20Cr, Cr Carbide Ni/Cr, Fe50Cr, for example)

Long-term steam oxidation rate and failure data have been generated that underpin the design and application processing work packages needed to develop and establish this technology for future and retrofit power generation plant.

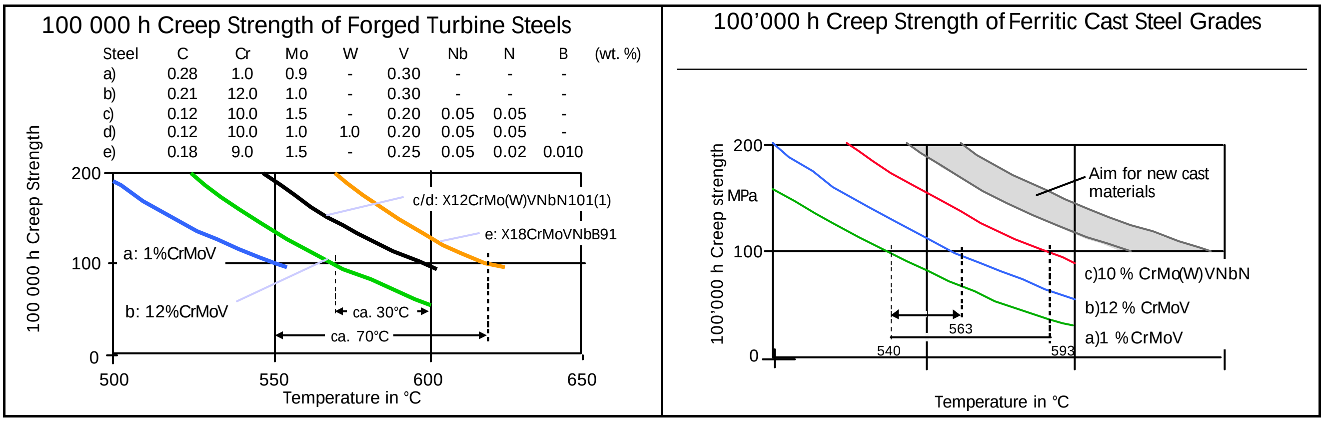


Figure 1. Development in creep strength capability of forged and cast steels (after [4]).

Steam Plant	Output MW_e	Live Steam bar / °C	Reheat Steam °C	Thermal Efficiency %
Skaerbaek	400	290 / 582	580 / 580	49
Nordiylland	400	290 / 582	580 / 580	48
Avedoere	530	300 / 582	600	47
Skopau A,B	450	285 / 545	560	40
Schwarze Pumpe A,B	800	264 / 542	560	40.6
Boxberg Q,R	818	260 / 540	580	41.7
Lippendorf R,S	900	268 / 554	583	42.3
Niederaussem	1050	265 / 576	600	>43
Isogo	600	251 / 600	610	>43
Westfalen (design study)	350	283 / 600	620	>43

Table 1. Summary of European Advanced Steam Power Plant (after [2]).

Project overview

The Brite EuRam FPV SUPERCOAT project is aimed at development and implementation of cost effective and environmentally friendly coatings technologies for steam power plant. By developing and validating oxidation protective coatings for the high creep strength ferritic steels used in current and future power plant installations the project aims to help facilitate the targeted rise in operating temperature from approximately 550 to 650°C to achieve increased efficiency and reduce operating costs. To achieve these objectives are number of work packages have been undertaken by the project partners, as summarised in Table 2. As indicated in Figure 2, eight partners from five EC countries have participated in the project. Table 3 summarises the various activities and contributions made by each of the partners.

The target components for coating application were identified as the main steam and hot reheat pipe system and headers, steam chest and control valve internals and the high pressure turbine stages. These parts are mainly thick-walled and made of either forged or cast ferritic-martensitic materials such as P91 or P92. These two alloys have been selected as the main substrate samples and a series of steam oxidation, mechanical property and thermophysical property tests on coated samples have been conducted and the degradation and failure mechanisms characterised and models developed aimed at simulating the breakdown in protective properties of the coatings during high temperature steam exposure. In addition to component demonstration tests and planned field tests with large components, the consortium has been able to take advantage of the KOMET650 programme at KW Westfalen power plant in Hamm, which has two specifically designed by-pass loops incorporated for materials testing purposes. As part of this programme, a number of coated and uncoated SUPERCOAT samples have been tested in live steam at temperatures ranging from 585 to 610°C.

WP 1. Mechanisms	Evaluation of oxidation and corrosion behaviour of uncoated and coated P91 and P92 samples. Aim to develop an improved understanding of oxide scale growth and coating degradation under high temperature steam.
WP 2. Coatings	Coating application trials, concentrating on slurry and HVOF deposition to large components to define optimal process conditions, quality control procedures and minimise costs. Smaller part coating trials using pack aluminising, electro less N-P and Ni-B, electroplating Cr & Ni and hybrid coatings have also been evaluated.
WP 3. Characterisation	Determination of mechanical and thermophysical properties of selected coatings (strain to failure, elastic modulus, bond strength, etc.,).
WP 4. Laboratory testing	Steam oxidation testing of uncoated and coated P91 and P92 coupons (650°C, ambient and 300 MPa pressure) under isothermal and thermal cycling conditions.
WP 5. Modelling	Prediction of scale formation and coating lifetime. Characterisation of interdiffusion between coating and substrate, analysis of chemistry and stability.
WP 6. Large component coating	Develop methods for coating and testing of steam pipes, chests and turbine parts. Demonstrate feasibility of coatings selected by application to components.
WP 7. Field tests	Selected coatings to be tested on components in a power plant.

Table 2. Summary of SUPERCOAT Work Packages.

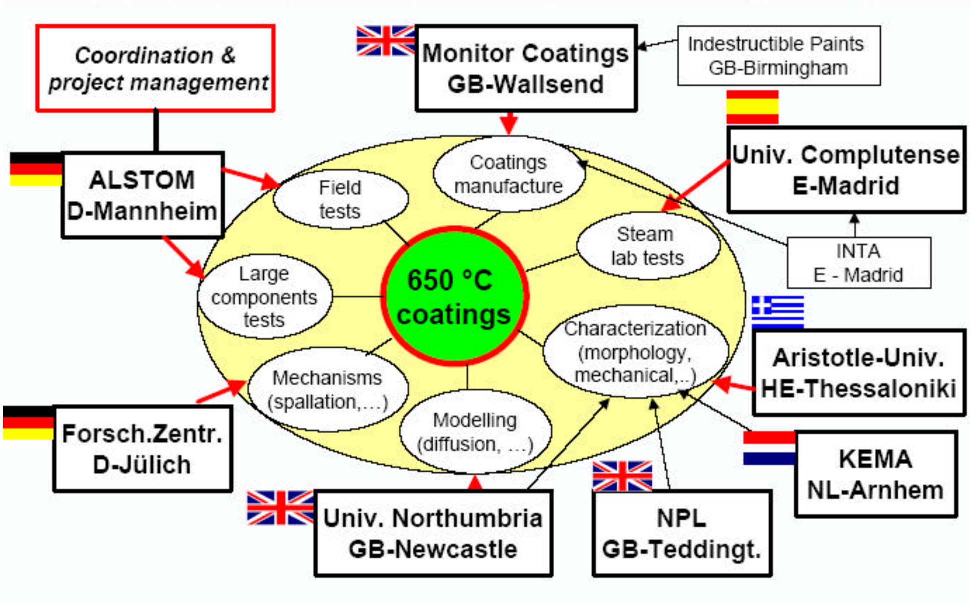


Figure 2. SUPERCOAT consortium (red arrows mark WP-leaders).

Coatings Development

To meet the demanding conditions experienced within an ultra-supercritical steam cycle (oxidation, solid particle erosion, high temperature and pressure cycling and variable chemical wear), the coating requirements have been summarised as follows:

- Passivation: formation of a protective oxide ceramic layer.

- Impervious to high temperature steam and free of open porosity.
- High resistance to ion-diffusion and high ohmic resistance.
- Coating and its passive layer insoluble in supercritical water.
- Superior adhesion to base material and similar thermal expansion coefficient as base material.
- High Erosion-resistance.
- Repairability.
- Thick layers feasible and sustainable.
- Lifetime should be at least 50,000 EOHs.
- Resistance against chemical agents used in power plant.

Partner	**Business Activity**	**Role in Project**
ALSTOM Power	OEM	**Co-ordinator.** Characterisation and long term testing. Field tests & supply of components. Implementation and exploitation.
Monitor Coatings Ltd	Coatings supplier	**WP2 Leader**. Thermal spray & slurry coating supplier, development and adaptation of coating processes & repair procedures.
NPL	RTO	Determination of mechanical properties and adhesion. Modelling of spallation and diffusion. Long term tests in steam under cyclic conditions.
Aristotle Univ. of Thessaloniki	University	**WP3 Leader.** Microstructural investigations, adhesion testing. Investigations into hybrid (duplex) coatings and boride coatings.
Univ. Complutense Madrid	University	**WP4 Leader.** Determination of coating properties & mechanisms of oxide formation. Lifetime modelling, scale fracture mechanics, surface modification.
FZ Jülich	RTO	**WP1 Leader.** Long term testing in different steam atmospheres, diffusion and thermodynamic modelling, characterisation, spallation mechanisms.
Northumbria University	University	**WP5 Leader.** Microstructural modelling, interdiffusion, thermodynamic calculations, characterisation (SEM, EDX, AFM), FE-calculations.
KEMA	RTO	Test facilities and laboratories, coating monitoring, NDT and creep phenomena.
Indestructible Paints Ltd.	Sub-contractor	Subcontract to Monitor Coatings Ltd., for slurry coatings & sealants.
Instituto Nacional de Técnica Aeroespacial (INTA)	Sub-contractor	Subcontract to Univ. Complutense. Supplier of slurry and HVOF coatings. Development of coatings, testing and characterisation.

Table 3. SUPERCOAT Consortium overview.

The coating classes identified to meet these demands consist of thermally sprayed metal powders and Cermets such as chromium carbide, and non-metallic inorganic coatings such as oxide-based overlay or aluminide based diffusion coatings applied using paint or sol-gel slurries. Figure 3 summarises the general scheme for differentiating between different strands of the coating development work plan for the programme. In general, each process aims to provide a barrier to oxygen contacting the steel surface by providing either a physical barrier that forms a stable protective layer but remains largely unreacted with the substrate, or else forms an integral protective layer diffused into the surface of the steel to provide a reservoir of aluminium for scale formation on top of the coating. Included within the coatings development work plan was an evaluation of binders, sealants, repair processes, hybrid coatings (plating and aluminising) and surface modification using borides.

Slurry coatings are suitable for internal and external application to small (e.g. blades) and large components (e.g., steam pipe, casings, valve internals) and can be relatively easily applied to complex shaped objects. HVOF deposition on the other hand, is a line of sight thermal spray process that is suitable for small and large parts, but application is mostly limited to external, regularly shaped surfaces. Most other deposition techniques (plating, CVD, PVD etc) are more or less limited to small component coating.

Following an extensive assessment of a number of candidate coatings using ambient and high pressure steam oxidation testing, as well as microstructural and mechanical evaluation, a down-selection of the most promising coatings was possible, as summarised in Table 4. Each of these coatings performed extremely well under steam oxidation and demonstrated adequate mechanical integrity and adhesion with the substrate. Figures 4 through to 7 show typical examples of the as-received microstructural sections through each of the down selected coatings listed in Table 4.

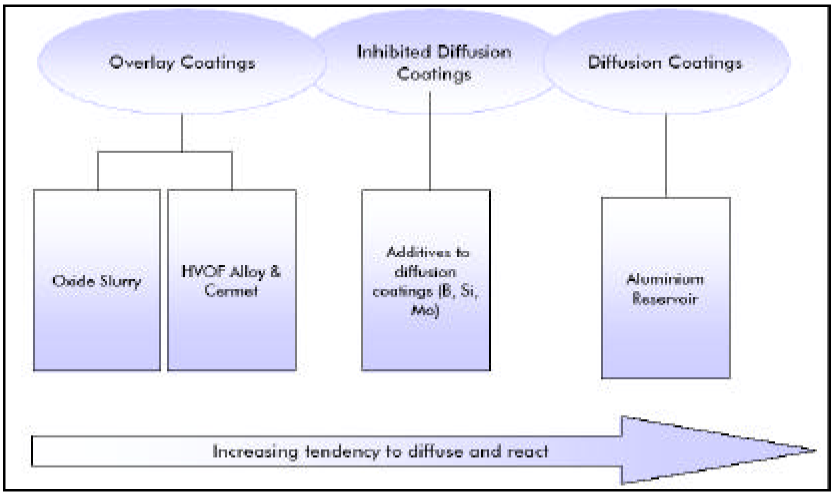


Figure 3. Classification of SUPERCOAT Coating systems

Number	Coating Type	Coating Name	Composition
1	Slurry	IPCOAT 9183	H3PP4, Cr2O3, Al, Phosphate binder
2	HVOF	Ni20Cr Powder	Cr min 20%, Ni(bal).
3	HVOF	Fe50Cr Powder	Cr min 50%, Fe(bal).
4	Pack Aluminide (PA)	Low Temp. PA	Al
5	Hybrid	ElCr PA	Cr, Al

Table 4. Summary of down-selected coatings for SUPERCOAT.

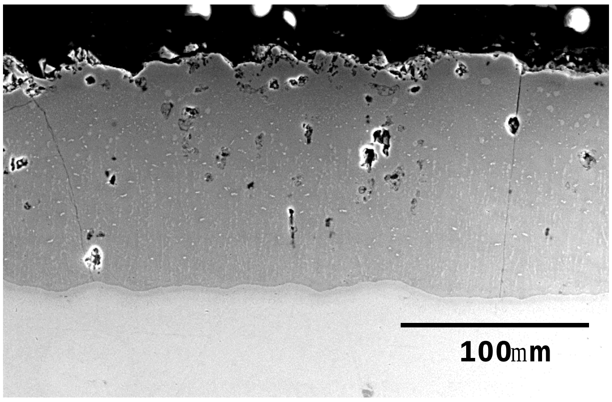


Figure 4. Diffused aluminide coating on P92 substrate.

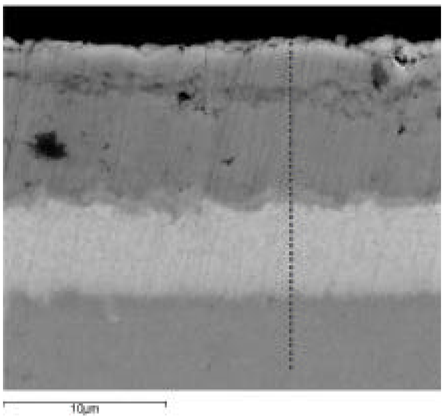


Figure 5. Hybrid aluminide coating on P92 substrate.

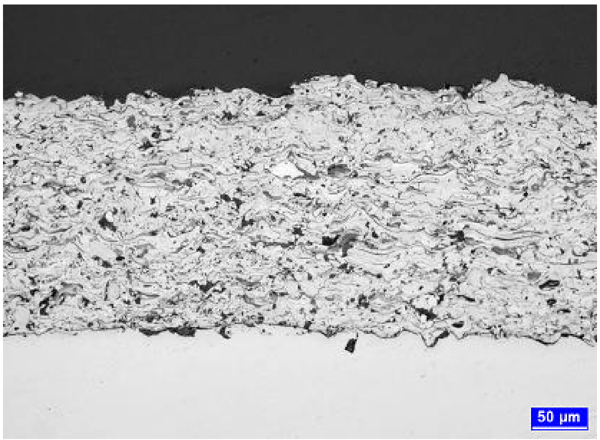


Figure 6. HVOF Ni20Cr coating on P92 substrate.

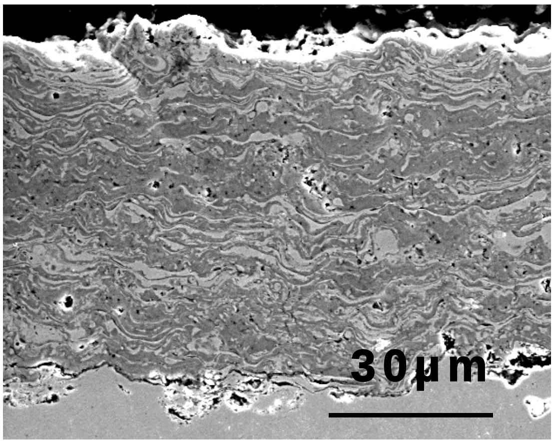


Figure 7. HVOF Fe50Cr coating on P92 substrate.

Concentration of effort on a more limited number of candidates has enabled further developments to be made and the application processes to be tailored to the needs of particular components identified by the manufacturer and suppliers within the programme. Additionally, new slurry formulations have also been developed that include metallic powder and boron additions, as well as silicate-free and chromium-free binders. A number of new HVOF coatings have also been evaluated based on FeAl, FeCr, FeCrAl and NiAl. Each has shown good processability and has been applied successfully to P91 coupons and have performed well under ambient steam oxidation testing. Additional slurry based coatings have also been prepared, such as overlay modified slurry aluminides, B modified diffusion aluminides and electroless Ni-diffusion aluminides. Surface preparation and heat treatment cycles (drying, curing, diffusion treatment as necessary) for the successful application of these coatings have been developed and the method of manufacture specified for the requisite quality documentation.

Steam Oxidation, Mechanical Testing and Characterisation

The main thrust of the experimental programme has been centred around preparation of a significant number of uncoated and coated P91 and P92 coupons for steam oxidation testing using gravimetric weight change analysis following incremental long term exposure under ambient and high pressure steam. In addition, samples for thermophysical property measurements (elastic modulus, thermal expansion coefficient, thermal diffusivity etc), strain to failure, ductile to brittle transition temperature and interfacial bond strength testing and residual stress measurements have been tested and the data compiled and applied within the modelling work packages. Both pre- and post-test exposure tests have been performed to assess the influence of thermal and steam exposure on coating durability and properties. Publications describing some of these activities can be found elsewhere [5 – 7].

The main objectives for the characterisation task have been to evaluate the pre- and post-exposure characteristics and effectiveness of the coatings using optical and electron microscopy (EDX and WDX), NDT (eddy current) and X-Ray diffraction and establish effective quality control documentation and procedures for manufacture and assessment of the coatings produced (thickness, uniformity, morphology, porosity, adhesion and composition). Post-exposure examination has concentrated on establishing the protection/degradation mechanisms (element redistribution, scale growth & thickness, porosity, spallation, etc), nature of the corrosion products and amount of metal loss suffered following steam exposure. In addition, mass spectrometry has been used to study in-situ the role of volatile species in the oxidation of P91 and P92 steels and coatings at 650°C at 1 bar pressure under a range of Ar-H_2O vapour mixtures (10 – 80% H_2O) in conjunction with gravimetric analyses of the kinetics of oxidation behaviour [8].

Steam Oxidation Testing

The steam oxidation testing conducted has formed the basis for the down selection of coatings produced within the programme. The objectives were firstly to define the test parameters such as temperature, gas composition, flow rate, length of exposure, etc., as summarised in Table 5, and conduct oxidation rig testing under flowing steam at atmospheric and high pressures. The test conditions were selected to simulate as close as possible those encountered in actual power plants and were based on prior laboratory test results [9]. Coating performance was determined by weight variation as a function of time and by microscopical analysis of exposed samples. Uncoated P92 and X20 steel coupons were tested by each of the partners as a means of benchmarking results generated by different test laboratories (ALSTOM, UNN, FZJ, UCM and INTA). Furthermore, thermal cycling tests have been performed by Aristotle University, Thessaloniki.

Temperature	650°C (long term tests >10,000 hrs) 800°C (accelerated tests <1,000 hrs)
Steam Composition	50% Ar, H_2O, de-oxygenated 100% H_2O, de-oxygenated
Flow Rate (ml/min)	1.7, 15.0, 33.3
Pressure	1 bar (long term tests >10,000 hrs) 300 bar (short term tests – 1,500 hrs)

Table 5. Summary of Supercritical Steam Oxidation test conditions

Figure 8 shows the general rig set up used by the partners for testing in pure, superheated steam at atmospheric pressure. Typically, this system works at ambient pressure at flow velocities between 150 and 300 ml/h. De-ionised water with no additives was used and by continuous bubbling nitrogen through the reservoir, the oxygen content of the steam was kept below 20 ppb. During the course of a test run, a series of weight change measurements were taken to monitor the behaviour of the samples and when a test was terminated the exposed samples were routinely sectioned for metallographic analysis. Figure 9 summarises the mass change curves obtained for P91 and P92 uncoated samples tested at 650°C, 1 bar supercritical steam with test results out to >10,000 hrs. The test results for P92 show good reproducibility, but also an accelerated oxidation rate compared with that for P91 as expected from previous results [10]. Figure 10a shows a typical example of a microsection through uncoated P92 after 2,300 hrs exposure to 1 bar supercritical steam at 650°C. A thick, multilayer oxide scale has developed on the surface of the steel that shows irregular internal features between the outer magnetite (Fe_3O_4) and inner Fe, Cr spinel layers and the development of sub-surface porosity adjacent to the steel. The overall thickness of the oxide scale is approximately 170 µm with significant depth of penetration into the steel.

In addition to the ambient pressure tests, a series of high-pressure steam oxidation tests have been carried out at 650°C and 300 bar pressure on behalf of the consortium by TU Darmstadt. The once-through design test facility is shown schematically in Figure 11. As for the ambient pressure tests, mass change measurements and metallographic characterisation have been conducted as a means of tracking the oxidation behaviour of the uncoated and coated P92 samples. In addition, a number of uncoated substrate samples have been tested for comparison (X20CrMoV11-1, Alloy 122, AISI 316 Ti, Inconel 625). The compositions are given in Table 6.

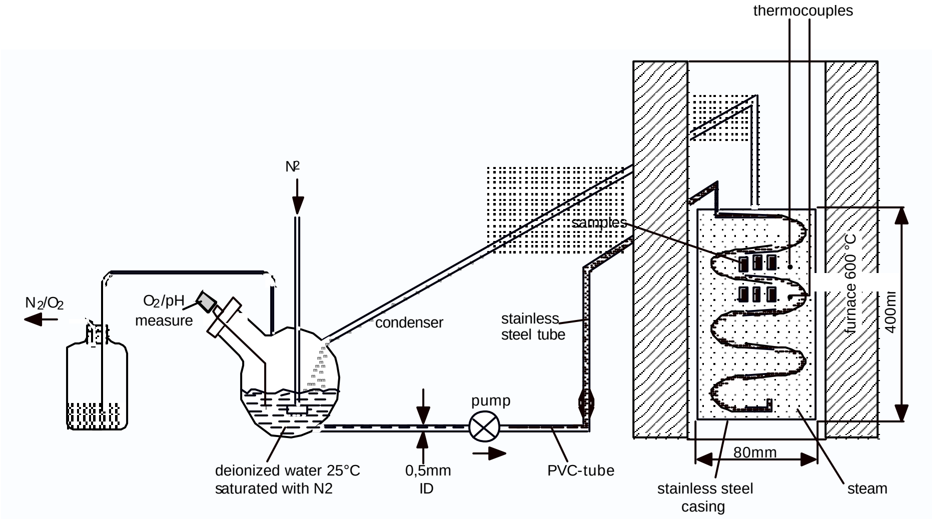


Figure 8. Schematic illustration of the atmospheric pressure, superheated steam test facility.

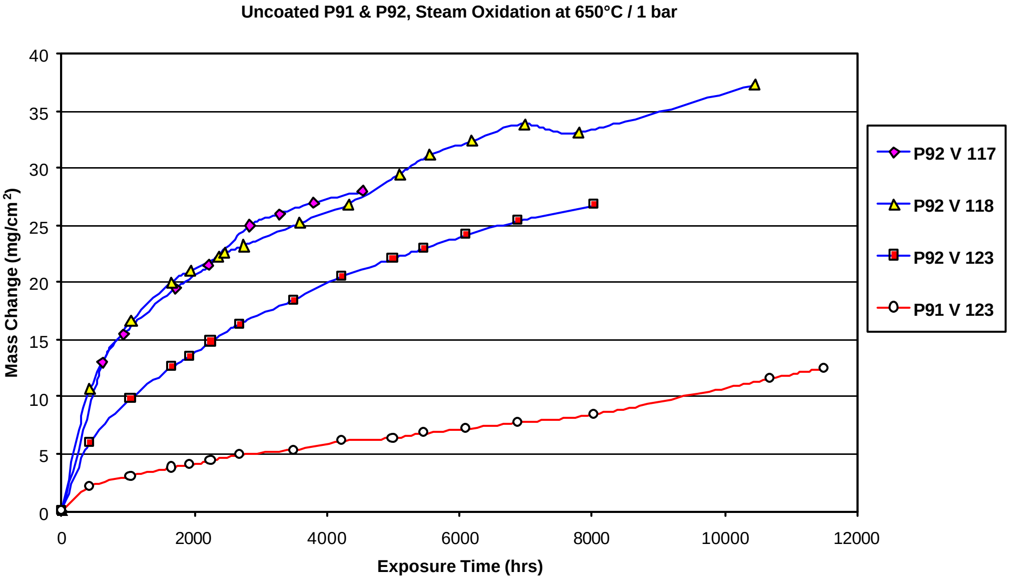


Figure 9. Mass change curves of uncoated P91 and P92 samples exposed to superheated steam at 1 bar, 650°C.

In most cases weight change measurements were found to be reasonably reproducible and in-line with expectations for the uncoated samples. Figure 12 shows the mass change test results for the uncoated samples exposed to 300 bar pressure steam at 650°C for test durations out to 1,500 hrs. The data show a consistent trend in terms of the effect of composition on oxidation resistance, ie., increased Cr content of the steel generally reduces the oxidation rate and the data show the clear advantage of austenitic stainless steels and nickel alloys under these environments (AISI 316 Ti & Inconel 625). The data also demonstrate the significant difference in oxidation resistance between P91 and P92.

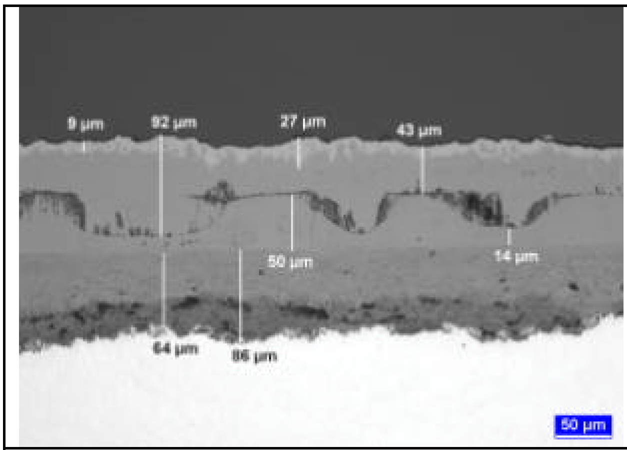


Figure 10a.Cross section through a P92 sample after 2,300 hours exposure to superheated steam at 1bar, 650°C.

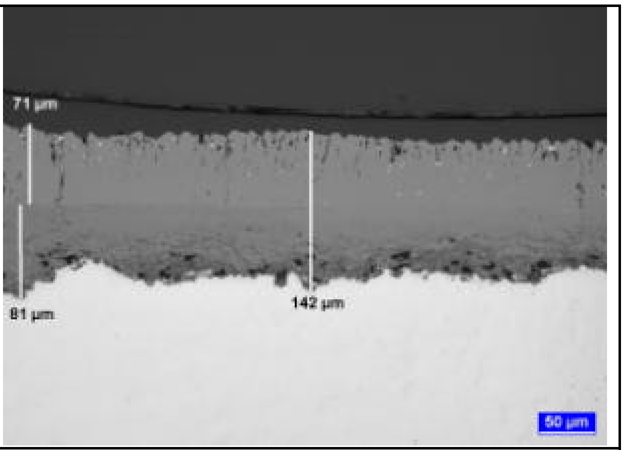
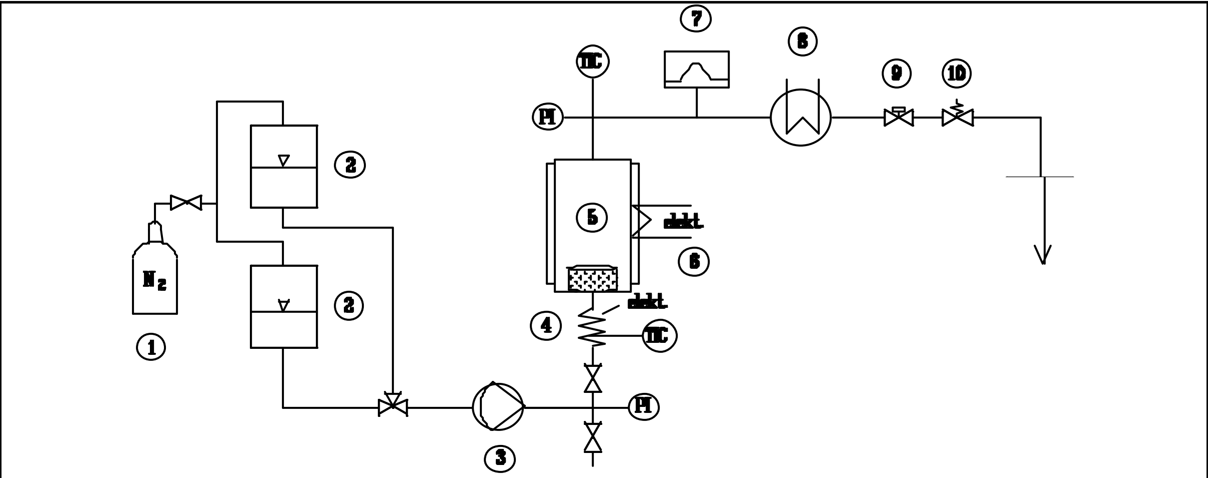


Figure 10b. Cross-section through P92 sample after 1,500 hrs exposure to HP steam at 300 bar, 650°C.



#	Item	Type / Manufacturer
1	Nitrogen	Linde, Specification 4.0
2	Feed water tank	Volume 16 litres
3	HP membrane pump	Orlita Mh/15/5, max. flow 30 g min^{-1}
4	Preheater	Time, ¼“-tube (Inconel 625®), toroidal transformer 3000 VA, 2 x 4 V
5	Autoclave	Self-made TU Darmstadt, Volume 250 ml, Inconel 625®
6	Trace heater	Philips, NiCr 80/20, heat length 600 cm, resistance 3,1 Ω
7	Burst disc	HIP, Linden Ave Erie PA, ¼“ (8412 psi)
8	Heat exchanger	Self-made, ¼“, Tube length 2 m
9	Control valve	HIP, Linden Ave Erie PA, ¼“
10	Overflow valve	Riegler, 1/8“ (red spring, 35 MPa)

Figure 11. High pressure steam oxidation test facility at TU Darmstadt for tests in supercritical water

Figure 10b shows a typical microsection through a P92 coupon following 1500 hrs exposure to 300 bar pressure steam at 650°C. The overall coating thickness is approximately 140 µm and shows a more regular internal structure to that seen at ambient pressure (see Figure 10a), though clearly a significant level of metal depth has been oxidised (inner and outer oxide scales are 81 and 71 µm respectively). An outer magnetite scale (Fe_3O_4) and an inner Cr-Fe-spinel have formed and the interface between the two scales remains unchanged during oxide growth. Thus, the magnetite grows at the interface to the steam by iron ions migrating through the two scales and taking-up oxygen from the steam. The spinel grows at the interface to the alloy by taking-up oxygen which migrates through the two scales [11].

Comparison of the ambient and high pressure test results for uncoated and coated samples revealed that for most of the coatings and base materials, the 1 bar test results provide a representative measure of the steam oxidation behaviour at higher pressures and can, therefore, be used for determining the oxidation behaviour and for general selection of candidate coatings. The weight gain curves for P92 at atmospheric pressure are very similar to those derived from high pressure testing (see Figures 9 and 12). This represents a key result for the test programme, however, for certain silica-based coatings that performed adequately well under ambient pressure steam, the high pressure trials confirmed the unsuitability of these coatings for steam turbine plant due to the solubility of SiO_2, which led to the rapid degradation of these coatings under HP steam.

Alloy	**Fe**	**Ni**	**Cr**	**W**	**Mo**	**Nb**	**C**	**Mn**	**Si**	**V**	**B**	**Others**
X20CrMoV11-1	Bal.	0.50*	11.5	2	0.45	0.07	0.1		0.50*	0.25	0.005*	0.04*Al, 0.02*P, 0.01*S
P91	Bal.	0.4	9	-	0.95	0.08	0.1	0.45	0.5*	0.2		0.04*Al, 0.02*P, 0.01*S
P92	Bal.	0.40*	9	1.75	0.45	0.065	0.1	0.45	0.50*	0.2	0.004	0.04*Al, 0.02*P, 0.01*S
Alloy122	Bal.	0.31	11.1	1.94	0.35	0.054	0.12	0.68	0.2	0.22	0.002	1.0Cu, 0.011Co, 0.005Al, 0.01*P, 0.007*S
AISI 316 Ti	Bal.	11.0	18.0	-	2.0		0.1*	<2.0				Ti = 5x%C
Inconel 625	5.0*	58	22		9	3.65#	0.1	0.50 *	0.50*			1.0*Co, 0.4*Ti. 0.4*Al, 0.015*P, 0.015*S

Table 6. Summary of compositions (mid-range for specification) of substrate steel and nickel samples tested under HP steam (* = max. # = plus Ta).

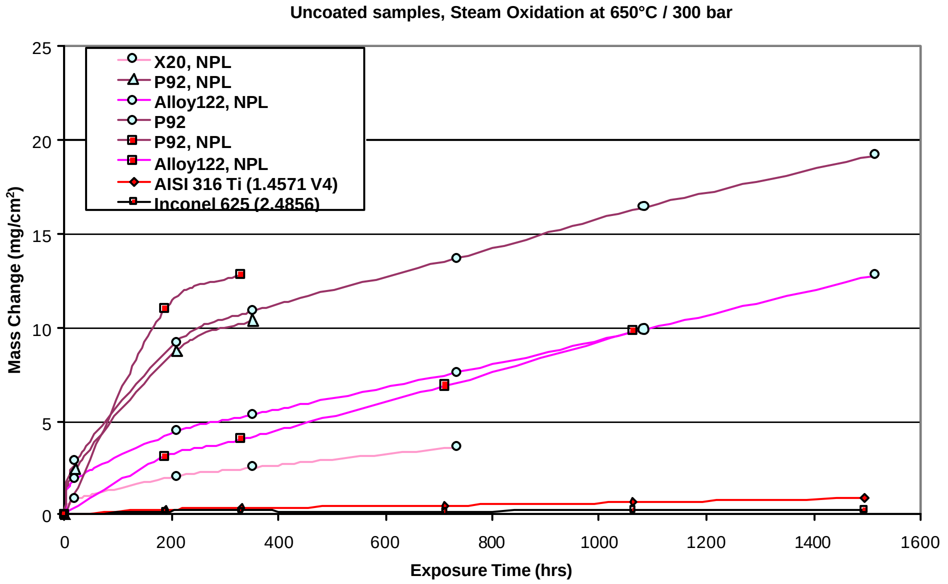


Figure 12. Mass change curves of uncoated substrates, exposed to supercritical steam at 300 bar, 650°C.

Steam oxidation weight change data for aluminised (diffused and overlay coating) and HVOF coated P92 samples are shown in Figures 13 and 14, respectively. In both cases, a significant reduction in oxidation rate is seen compared with uncoated P92, in particular for the diffused aluminide and HVOF Ni20Cr samples. The test data shown for overlay aluminide coatings demonstrate the need for an effective seal coat to prevent ingress of HP steam to the steel surface.

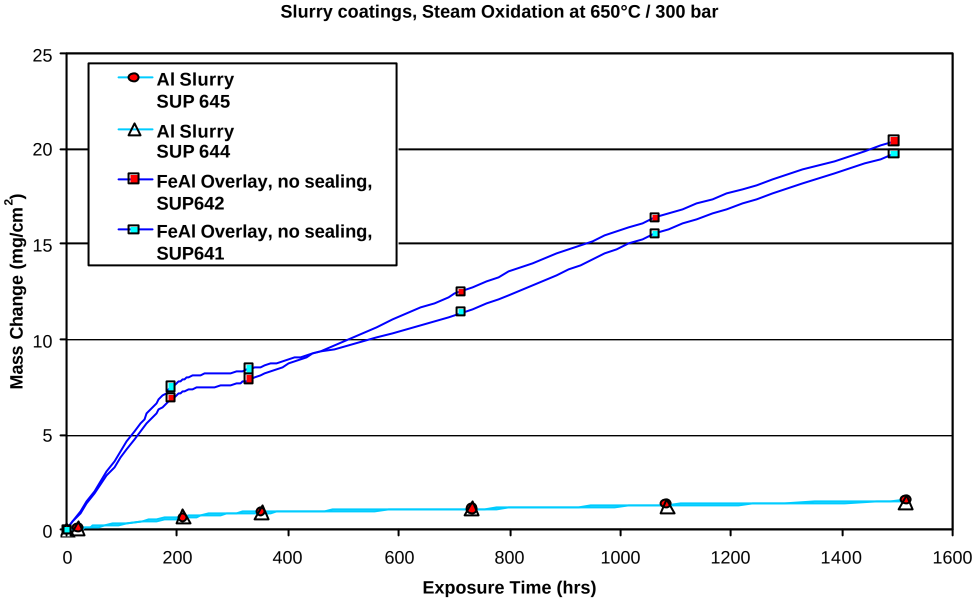


Figure 13. Mass change curves for aluminium slurry coated P92 coupons, exposed to supercritical steam at 300 bar, 650°C (SUP 645 & 644 are diffused coatings).

Another key result for the programme has been the excellent performance found under both ambient and high pressure steam for the Ni20Cr (Figure 14) and the Al-diffusion coatings (slurry deposition and pack aluminised variants – Figure 13) produced within the programme and has enabled the down-selection of suitable candidates given in Table 4. The data for diffused aluminide coatings have been substantiated by long term results, provided by INTA from COST522, on the behaviour of slurry aluminides under ambient pressure steam at 650°C and indicate that these coatings offer the potential for long-term protection against steam oxidation. The long-term data for a slurry aluminide are compared with those for uncoated P92 in Figure 15 (coated sample test results out beyond 35,000 hrs) and a significant difference in oxidation behaviour is observed. Figure 16 shows a microsection through a typical diffused aluminide coated sample after 20,000 hours of test exposure. By comparison with Figure 4, the coating can be seen to have developed a degree of interfacial porosity (Kirkendal interdiffusion between Fe and Al), but has remained intact to form an effective barrier to oxidation of the steel. A secondary reaction zone is also evident immediately below the coating that shows evidence of coarse AlN precipitates, which may indicate the presence of a weakened zone immediately beneath the coating surface (reduced nitride strengthening of the steel). The impact of sub-surface depletion of alloy constituents due to oxidation on the mechanical properties of these steels has been reported previously [12]. Microhardness measurements taken within the current programme show a reduction in hardness of the steel adjacent to the secondary zone after 20,000 hrs exposure, but also indicate a softening of the aluminide coating itself as the level of aluminium in the coating is depleted due to external oxidation and internal diffusion to the steel.

Impact Fatigue Testing of Coated P92 Samples

Impact fatigue testing has been conducted at room temperature as a means of evaluating the fatigue strength of the coatings produced within the programme [13 - 16]. Using this method, the surface of the coated specimen is cyclically loaded by repetitive impacts applied using a hard ball indenter until coating failure occurs. The Hertzian pressure field developed induces a complex stress field both within the coating and at the interface with the substrate. These stress states are responsible for inducing distinct failure modes, either within the coating or at the interface and generates realistic structural transformation within the coating by means of fatigue crack initiation and growth phenomena, which are responsible for the gradual micro chipping and degradation of the coating. The impact testing facility is shown in Figure 17 and Figure 18 illustrates the form of the indent impression and the means by which typical indents are analysed as the number of impact cycles accumulates. The impact crater is examined using an SEM for microcracking and the constituent elements of the coating and substrate are identified using EDX analysis as illustrated.

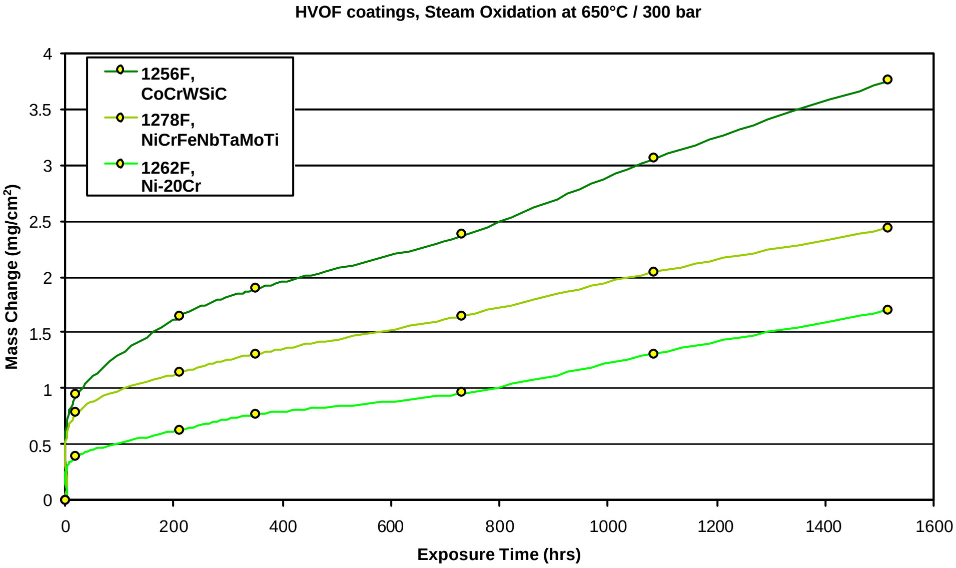


Figure 14. Mass change curves for HVOF metal powder and Cermet coated P92 coupons, exposed to supercritical steam at 300 bar, 650°C.

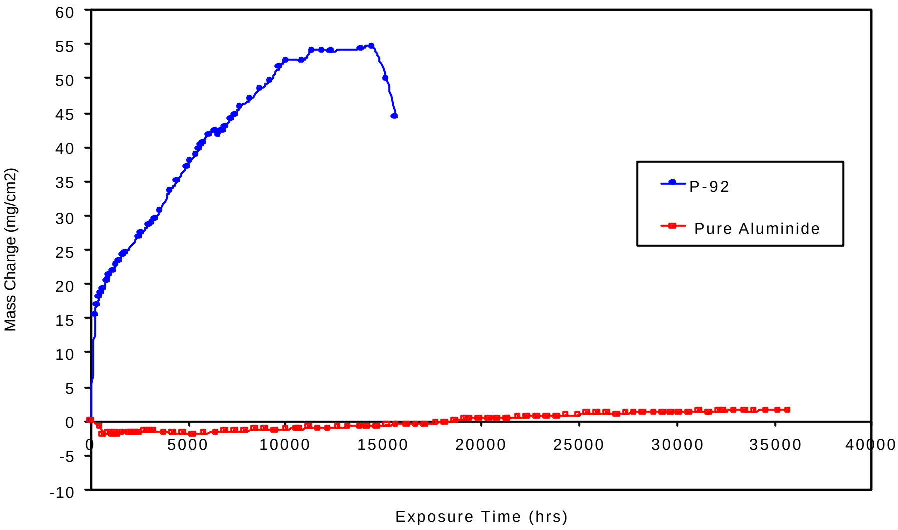


Figure 15. Mass change curves for HVOF metal powder and Cermet coated P92 coupons, exposed to supercritical steam at 300 bar, 650°C.

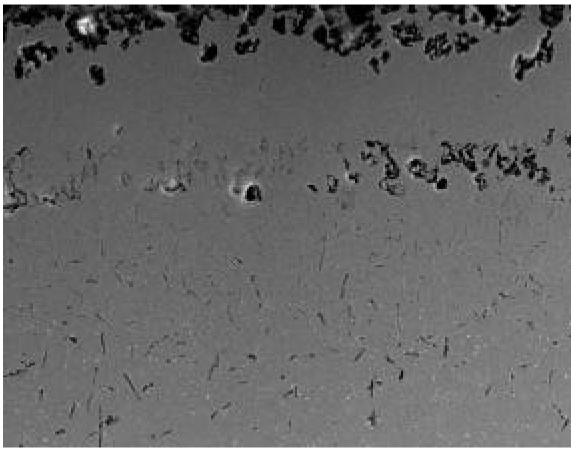


Figure 16. Diffused aluminide coating after 20,000 hours exposure to ambient pressure steam at 650°C.

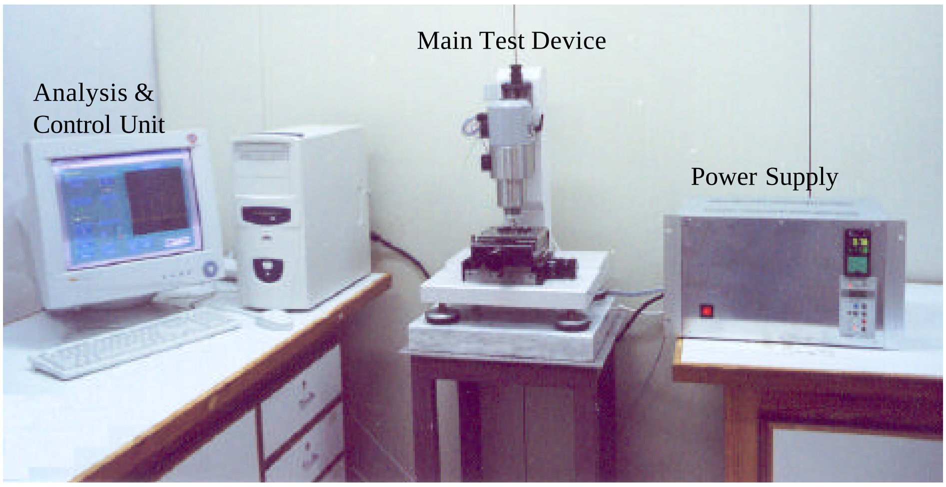


Figure 17. Impact testing system.

Figure 19 shows the fatigue endurance curves (impact load vs. cycles to failure) generated for a number of coatings tested at room temperature using the impact fatigue test method. Under these loading conditions the HVOF sprayed coating WC-CoCr shows superior fatigue threshold and strength to both the Ni20Cr, CrC-Ni25Cr and diffused aluminide coatings (SUP86, SCOAT & SUP76). The slurry overlay type coatings (MB1, MAC1-C and MX1) show an intermediate fatigue threshold level. The pack aluminised coating SCOAT was found to have the lowest fatigue endurance of the coatings tested.

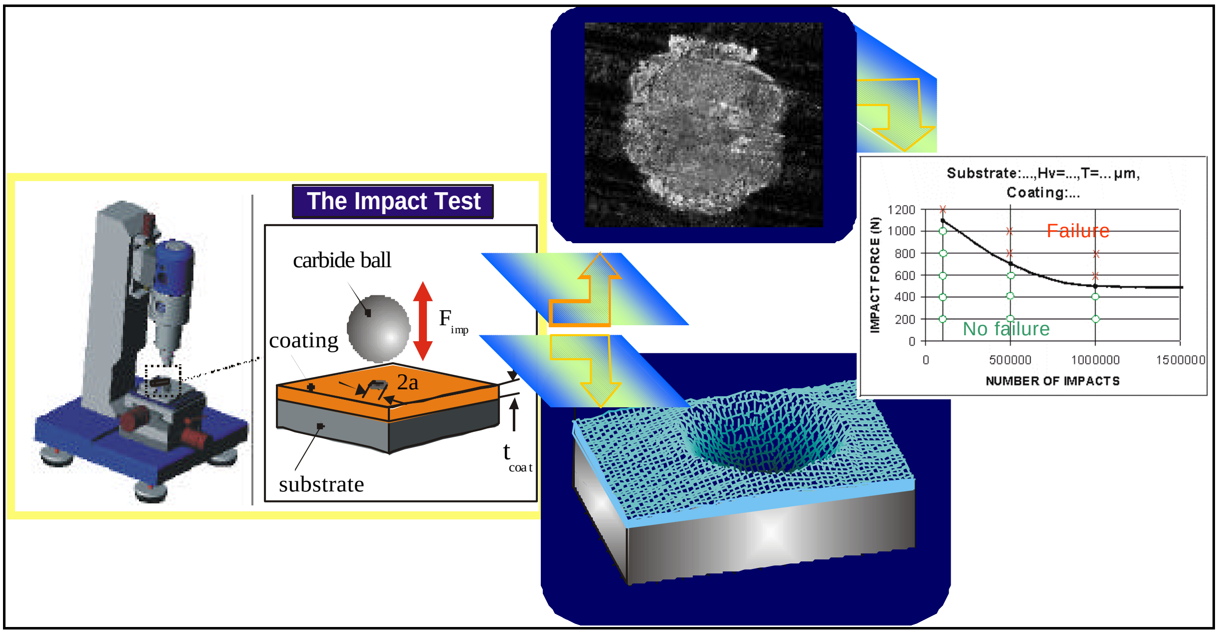


Figure 18. Schematic illustration of impact fatigue endurance and failure mode determination.

Mechanisms and Characterisation

The objectives for this work package were to develop an improved understanding of the mechanisms of scale formation and growth, oxidation protection and the processes responsible for degradation during high temperature exposure. The influence of thermal exposure and cycling on the scale formation and degradation mechanisms such as spallation and breakdown of protective oxide layers have been investigated, as well as interdiffusion of coating and substrate alloying constituents, solution of coating material in supercritical water (hydrothermal processes, e.g. in the case of silicates) and phase change processes. The most important degradation mechanism in the case of aluminide forming coatings is diffusion of Al into the substrate material, though for some protective layers volatility is a critical issue as the solution of the coating material by supercritical water was observed, which has been shown to be heavily dependant on the pressure.

Figure 20 shows a typical examination conducted on an HVOF Ni20Cr coating applied to P92 and examined using optical and electron microscopic and EDX analysis techniques. A thin, external chromia scale was found on the coating surface that formed an adherent and stable protective film. Alumina particles were also found at the metal/coating interface, which also showed evidence of a non-continuous chromia layer. Some evidence of Cr-rich particles was also evident as indicated. No evidence of cracking within the coating or along the interface was found and these coatings were seen to provide a stable, protective barrier to the ingress of steam to the steel surface. As a footnote to the experimental measurements made on small coupons, it is evident that the majority of the weight gain measured for the HVOF Ni20Cr samples was due to oxidation of the steel at or around the support hole drilled into the samples, which are difficult to coat using HVOF processes.

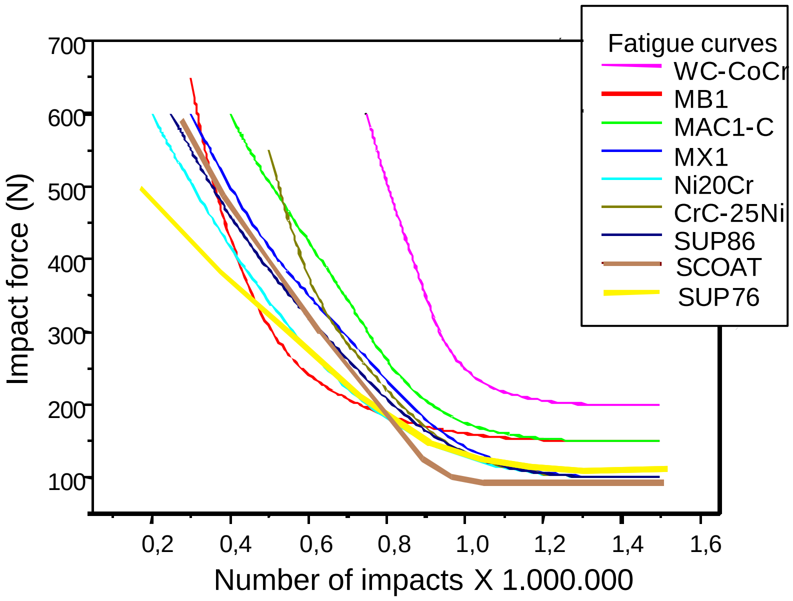


Figure 19. Impact fatigue endurance curves for HVOF and slurry aluminide coated P92 at room temperature.

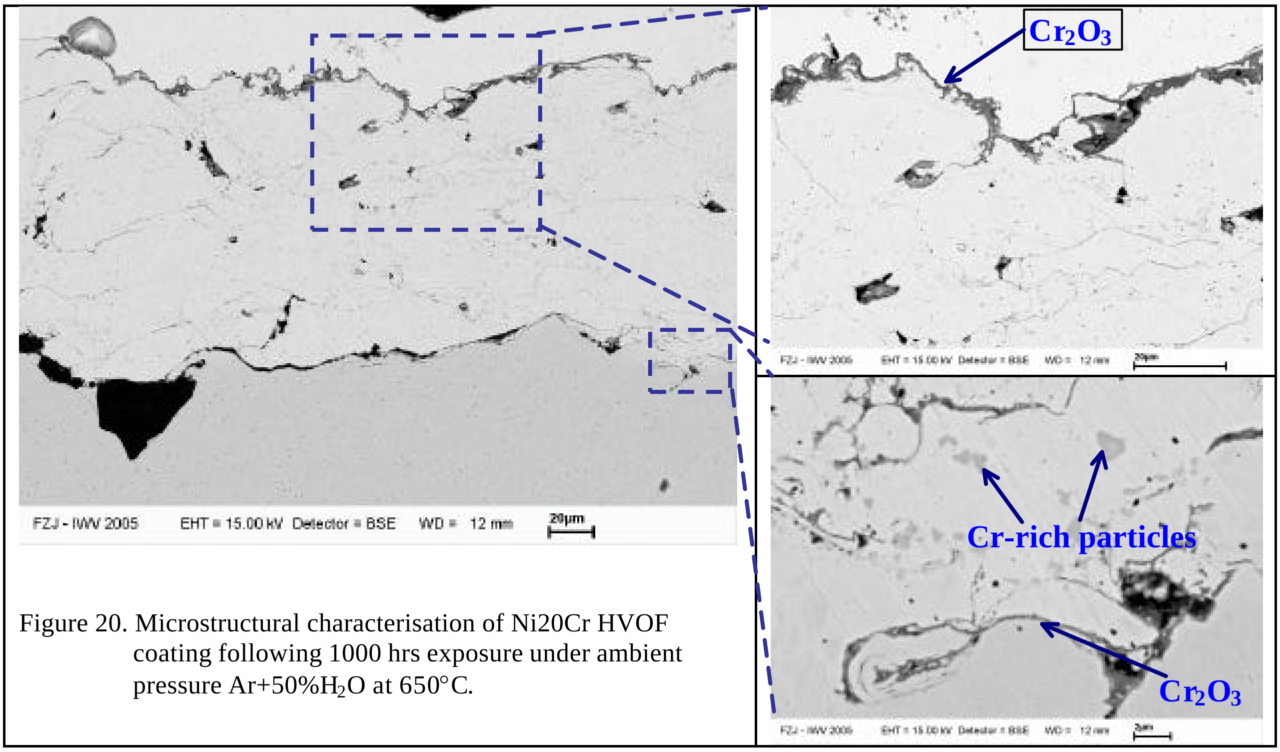


Figure 20. Microstructural characterisation of Ni20Cr HVOF coating following 1000 hrs exposure under ambient pressure Ar+50%H_2O at 650°C.

Modelling

The objectives for the SUPERCOAT modelling work package are to develop models based on the experimental observations to predict scale formation, scale growth, interdiffusion, phase stability (thermodynamic and kinetic), scale deformation and fracture and enable better design choices to be made in the development of high performance coatings for protection against steam oxidation. A number of modelling tools have been applied, including DICTRA and Darken (diffusion modelling) and ThermoCalc (thermodynamic phase equilibria calculations) in simulating the phase stability and interdiffusion of the coating layers with the substrate steels. FE calculations of the thermal stresses generated within the protective scale and underlying coating layer have been performed using ABAQUS. This work has not been reported in detail in the present paper, but will be presented at a later date.

Component coating trials

The objectives for the component coating trials are to specify the optimal composition and establish the method of manufacture and industrialise the process suitable for large steam power plant components. Further optimisation will be conducted following industrial assessments (surface preparation, composition and coating processes) and establish methods for quality control of the coatings on large components. A number of actual and sub-scale components have been coated as a means of demonstrating the feasibility of oxidation protective coatings for steam turbine power generation plant. To date, several steam turbine blades have been coated using pack aluminising, slurry aluminising and HVOF deposition of Ni20Cr, Cr Carbide Ni/Cr and Fe50Cr powders. Figure 21 shows a typical example of a coated turbine blade following surface tumbling treatment and examples of the microsections taken through the leading edge section of the blade. Presently, a large section of 400 mm diameter P92 steam pipe is being prepared for coating application (aluminised inner surface) and will be evaluated by means of NDT, sectioning and weldability trials. In addition, a number of small-scale tubes have been coated (aluminised inner walls and HVOF Ni20Cr or Fe50Cr applied to the outer surfaces) for field testing as part of the KOMET650 programme in the power plant KW Westfalen in Hamm.

Field trials

The objectives for the field tests were to validate the laboratory test results in operating plants using small test specimens (KOMET650 stub samples as shown in Figure 22), as well as larger components if possible and enable further assessment and optimisation of the coatings to be achieved. The field tests within the KOMET project are carried out in two test bypass tubes at different pressures and temperatures. Conditions in the high temperature bypass are on average 630°C, 180 bar and in the “low temperature” bypass 595°C, 96 bar. Coated samples (HVOF and slurry based) have been tested at KW Westfalen and removed periodically for inspection over the last two years. The exposure started in August 2003, however, due to plant shut-down the exposure periods have been subject to interruption. This work is continuing with results expected for the beginning / mid of 2006.

Conclusions

1. A brief review and assessment of the Framework V Brite EuRam project SUPERCOAT has been provided.
2. To enable the specification of oxidation resistant coatings for supercritical steam power plant applications, a significant number of uncoated and coated P91 and P92 samples have been prepared and tested under steam oxidising conditions. In addition, a range of mechanical and thermophysical property tests have been conducted on coated samples. These data have been used to down select the most promising candidate coatings for further development and industrialisation studies.
3. Ambient and high pressure steam oxidation tests have been conducted at 650°C. Diffused and pack aluminide coatings and HVOF Cermet and metallic powder coatings have all shown promising results in providing reduced steam oxidation rates under ambient and high pressure steam at 650°C.
4. An in-depth study of oxide scale formation and coating degradation and failure mechanisms has been conducted by means of mechanical testing and optical and electron microscopy. These analyses have been used to inform the coating down selection and the development of materials models for prediction of coating degradation and spallation lifetime. Mechanisms of protection and degradation have been identified.
5. Coating process industrialisation and validation has been achieved and continues with application of diffused and pack aluminised and HVOF coatings to components (turbine blades, steam pipe) and field test specimens

(test stubs, tubes). Metallographic inspection and characterisation have been used to inform development of quality standards and improved processes.

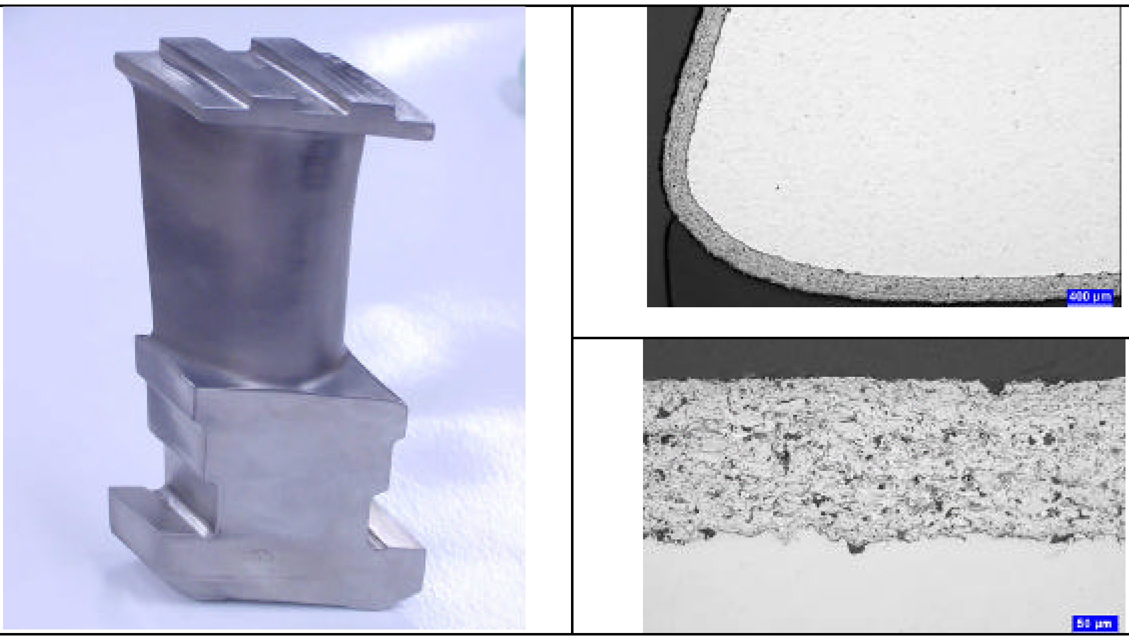


Figure 21. Typical example of HVOF Cr Carbide Ni/Cr coated steam turbine blade.

Figure 22. KOMET650 test stubs and carrier (left) prior to assembly and insertion in by-pass loop (right).

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