BOILER MATERIALS FOR ULTRASUPERCRITICAL COAL POWER PLANTS

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Executive Summary

A. Project Objective

The principal objective of this project is to develop materials technology for use in ultrasupercritical (USC) plant boilers capable of operating with 760°C (1400°F), 35 MPa (5000 psi) steam.

B. Background and Relevance

In the 21st century, the world faces the critical challenge of providing abundant, cheap electricity to meet the needs of a growing global population while at the same time preserving environmental values. Most studies of this issue conclude that a robust portfolio of generation technologies and fuels should be developed to assure that the United States will have adequate electricity supplies in a variety of possible future scenarios.

The use of coal for electricity generation poses a unique set of challenges. On the one hand, coal is plentiful and available at low cost in much of the world, notably in the U.S., China, and India. Countries with large coal reserves will want to develop them to foster economic growth and energy security. On the other hand, traditional methods of coal combustion emit pollutants and CO2 at high levels relative to other generation options. Maintaining coal as a generation option in the 21st century will require methods for addressing these environmental issues.

This project has established a government/industry consortium to undertake a five-year effort to evaluate and develop of advanced materials that allow the use of advanced steam cycles in coal-based power plants. These advanced cycles, with steam temperatures up to 760°C, will increase the efficiency of coal-fired boilers from an average of 35% efficiency (current domestic fleet) to 47% (HHV). This efficiency increase will enable coal-fired power plants to generate electricity at competitive rates (irrespective of fuel costs) while reducing CO2 and other fuel-related emissions by as much as 29%.

Success in achieving these objectives will support a number of broader goals. First, from a national prospective, the program will identify advanced materials that will make it possible to maintain a cost-competitive, environmentally acceptable coal-based electric generation option. High sulfur coals will specifically benefit in this respect by having these advanced materials evaluated in high-sulfur coal firing conditions and from the significant reductions in waste generation inherent in the increased operational efficiency. Second, from a national prospective, the results of this program will enable domestic boiler manufacturers to successfully compete in world markets for building high-efficiency coal-fired power plants.

The project is based on an R&D plan developed by the Electric Power Research Institute (EPRI) that supplements the recommendations of several DOE workshops on the subject of advanced materials, and DOE's Vision 21. In view of the variety of skills and expertise required for the successful completion of the proposed work, a consortium that includes EPRI and the major domestic boiler manufacturers (Alstom Power, Babcock and Wilcox (a division of McDermott Technologies Inc.), Foster Wheeler and Babcock Borsig Power) has been developed.

C. Project Tasks

The project objective is expected to be achieved through 9 tasks as listed below:

Task 1.	Conceptual Design and Economic Analysis
Task 2.	Mechanical Properties of Advanced Alloys
Task 3.	Steamside Oxidation Resistance
Task 4.	Fireside Corrosion Resistance
Task 5.	Welding Development
Task 6.	Fabricability
Task 7.	Coatings
Task 8.	Design Data and Rules
Task 9.	Project Integration and Management

D. Major Accomplishments During the Quarter

- Initial results from long-term creep rupture testing for Super 304H, HR6W, Alloy 230, and Alloy CCA617 are available. Alloys Super 304H and Haynes 230 appear to meet expectations, HR6W is below expectations, and Alloy CCA617 is exceeding expectations.

- Material aging tests are underway at the University of Cincinnati and ORNL.

- The first two exposures for steam side oxidation were completed. Evaluation of coupons including weight gain and metallographic analysis has been performed. Exfoliation was observed in some of the ferritic coupons. Chromium content was clearly shown to have an overriding effect on the oxidation behavior of all but one of the materials.

- Procurement of samples for the fireside corrosion retort testing is almost complete with only five materials not purchased and only one found to be unavailable so far.

- Xcelenergy, TVA, FirstEnergy, AEP and CINERGY have indicated interest in being a host for a corrosion probe.

- Test loops for steam loops at Reliant's Niles Plant successfully passed hydro testing and were sent to the plant. All erection and arrangement drawings were finalized.

- Welding trials on Super 304H and CCA617 were successful using the GTAW process but other processes were not successful.
- A tapered tube specimen was determined to be the best configuration for analyzing strain damage. Due to the high force required to prepare these samples, Foster Wheeler will perform all straining.
- Weld clad tube samples were successfully prepared using Inconel 52, 72, and 622 filler metals.
- Spreadsheets have been prepared to share data between the different participants in the project.
- A topical report on Reference Stress Method was completed and issued.

E. Plans for the Next Quarter

It is anticipated that the following work will be completed during the next quarter:

- Issue report “Assessment of the Alloy Performance Requirements” part1.
- Begin 100-hour preliminary testing of fireside corrosion retort.
- Finalize three host utilities for corrosion probe installation.
- Perform welding tests on HR6W and SAVE 12 materials.
- Fabrication testing will begin on HR6W and SAVE12.

F. Issues

- We have not been able to secure three different utilities for corrosion test probe installation. Talks are ongoing with several utilities.
- Delivery of filler metal for Inconel 740 continues to be a problem. Development schedules are slipping.
- Welding of nickel based alloys with high deposition welding processes like SAW or GMAW may not be possible.
- Lead investigators for Task 8 have not been identified for several sub tasks.

2.0 Taskwise Status

Task 1
Conceptual Design and Economic Analysis
(Task lead EPRI)

- The objective of Task 1 is to specify the temperature/pressure distribution for 760°C/35 MPa (1400°F/5000 psi) steam inlet conditions so that the data needs and the range of test parameters can be identified and the economics of material selection established.

Task 1A: Alstom Approach (Alstom Power Co.)

Objectives

The primary objectives of this subtask are:

- Develop a conceptual boiler design for a high efficiency ultra supercritical cycle designed for 1400F steam temperature.
- Identify tubing and piping materials needed for high temperature surface construction.
- Estimate gas and steam temperature profiles so that appropriate mechanical, corrosion and manufacturing tests of materials could be designed and conducted to prove suitability of the selected alloys.

Progress for the Task

A final report has been completed and distributed.

Task 1B: Babcock Approach

Objective

The objectives of this subtask are the same as in Subtask 1A.

Progress for the Quarter

Due to lowering of allowable stresses for In 740, a re-evaluation of the design for an Ultra Supercritical Boiler was warranted. The difference in allowables is shown in figure 1 below.

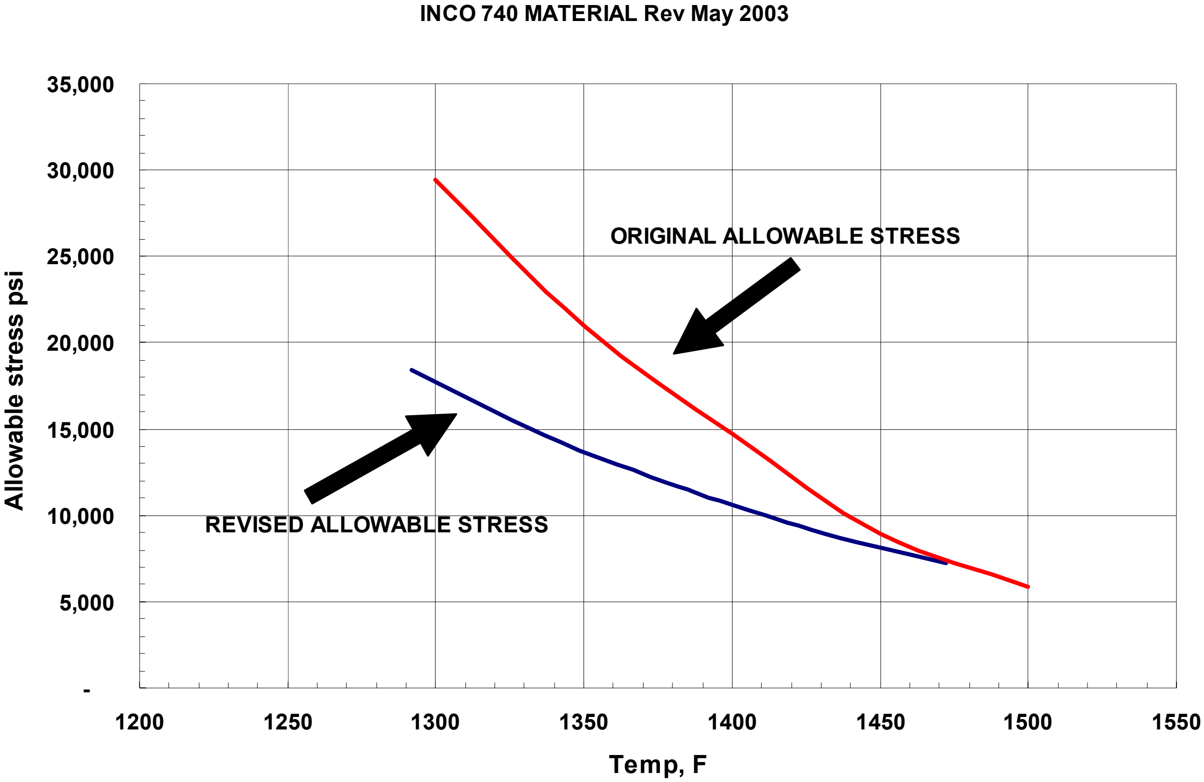

Figure 1: Difference in original allowable stress and revised allowable stress for In 740 material.

The primary component affected by the lowering of allowable stresses was the superheat outlet headers. The original design called for two headers 3.3" thick with a 24.4" OD and end outlets. This design is easier and less expensive to manufacture. The thickness limit was about as high as desired from a cycling standpoint. To keep this as the maximum thickness the outside diameter of the headers had to be reduced to meet the lower allowables. The smaller OD required the installation of outlet tees in the center of the headers to have enough area for the steam flow required. This will add to the cost of the boiler but will not have an effect on unit capacity or efficiency. Thicker tubing and reheat headers will also be required due to the reduced allowable stress for In 740.

Concerns

None.

Plans for the Next quarter

None.

Task 1C: Economic Analysis

Objective

The objective of this task is to determine relative economics of the USC plant.

Progress for the Task

A final report has been completed and distributed.

Task 2
Mechanical Properties of Advanced Alloys
(ORNL)

The objective of Task 2 is to produce the mechanical properties database needed to design a boiler to operate at the steam conditions within the scope of the project.

Task 2A: Assessment of the Alloy Performance Requirements

This assessment will focus on performance needed for boiler service in the temperature range of 649°C (1200°F) to 871°C (1600°F) and will produce a report that justifies the materials selected for the pressure retention components of the USC steam boiler.

The first part of the assessment report has been drafted and provides an overview identifying the materials selected by the consortium and gives an indication of the scope of the mechanical testing work to meet the project needs. The draft is being configured to the EPRI format and will be sent for review in October. The second part, dealing with 9-12% chromium steels, is being configured to the EPRI format and will be ready for steering committee review in October. The third and fourth parts, dealing with austenitic iron-bearing alloys and nickel base alloys, are still in the draft form.

Task 2B: Detailed Test Plan

The detailed mechanical properties test plan is intended to provide guidance on the scope of the mechanical testing for each material to support of resolution of issues related to the tasks undertaken in the project. Categories include mechanical characterization, data production for the development of code cases, effects of fabrication variables, weldment performance, fatigue and thermal-fatigue behavior and the like. To some measure, the test plan is still evolving.

The characterization testing plans have been completed for four of the six materials in the project (Super 304H tubing, HR6W tubing, alloy 230 tubing, and CCA617 tubing). The creep-rupture database for Super 304H stainless steel and alloy 230 was judged to be adequate, since both materials are code alloys.

The testing plans for HR6W, SAVE 12, CCA617, and Inconel 740 are expected to be more expansive, since code cases will be needed if these materials are used. The testing plan for the thick-section materials is still under development.

Task 2C: Long Term Creep Strength

The objective of the long-term creep testing is to identify the general characteristics of the creep and damage accumulation in the candidate alloys.

The status for the four alloys currently in testing is provided in the tables below. In each table, comparison of the rupture lives may be made with the expected life based on prior data. The initial results indicate that the strength of the Super 304H and alloy 230 are meeting expectations while the HR6W is below expectations. The CCA617 alloy is exceeding expectations that are based on performance equivalent to alloy 617.

The lower strength in weldments for alloy 230 is typical of the alloy.

SUPER 304H SS

TN	SN	Temperature (Deg. C)	Stress (MPa)	Expected Life (h)	Start	Life (h)
30298	1	600	240	10000	6/11/2003	
30299	2	600	280	1000	6/11/2003	
	3	600	340	100		
30293	4	650	120	10000	6/3/2003	
30292	5	650	210	1000	6/3/2003	2240
	6	650	260	100		
	7	700	110	10000		
30294	8	700	160	1000	6/3/2003	1011.5
	9	700	210	100		

HR6W

TN	SN	Temperature (Deg. C)	Stress (MPa)	Expected Life (h)	Start	Life (h)
30282	1	650	200	1000	5/21/2003	921.1
30315	2	650	175	6000	7/2/2003	2194.2
30330	3	650	150	20000	7/31/2003	
	4	675	200	500		
	5	675	170	1000		
	6	675	150	6000		
	7	700	200	50		
	8	700	170	500		
30317	9	700	150	1000	7/9/2003	451.3
30325	10	700	120	10000	7/22/2003	
	11	725	170	50		
30283	12	725	150	500	5/21/2003	187.5
30291	13	725	120	5000	6/2/2003	723.8
	14	750	140	100		
	15	750	120	500		
	16	750	100	5000		
	17	750	85	20000		
	18	775	100	600		
	19	775	85	5000		
	20	800	100	150		
	21	800	85	1000		

Alloy 230

TN	SN	Temperature (Deg. C)	Stress (Mpa)	Expected Life (h)	Start	Life (h)
30302	1	650	350	200	6/16/2003	410.8
30306	2	650	300	1000	6/18/2003	1071.4
	3	650	200	10000		
	4	700	300	100		
30301	5	700	200	1500	6/12/2003	1517.1
	6	700	140	15000		
	7	750	200	100		
	8	750	140	2000		
	9	750	100	15000		
	10	800	140	100		
30300	11	800	100	2000	6/11/2003	2101.2
	12	800	80	20000		
30311	W01	650	350	200	6/26/2003	84.9
30290	W02	650	300	1000	7/8/2003	825.4
30313	W03	700	399	100	7/1/2003	22.7
30319	W04	700	200	1500	7/10/2003	207.1
30320	W05	750	200	100	7/14/2003	30.7
30327	W06	750	140	2000	7/23/2003	170.6
30328	W07	650	200	10000	7/24/2003	1550.6
30332	W08	700	140	15000	8/6/2003	

Alloy CCA617

TN	SN	Temperature (Deg. C)	Stress (Mpa)	Expected Life (h)	Start	Life (h)
30352	13	650	400		9/10/2003	
30303	1	650	350	200	6/16/2003	
30305	2	650	300	1000	6/18/2003	
30357	3	650	200	10000	9/16/2003	
30337	4	700	300	100	8/19/2003	
30318	5	700	200	1500	7/9/2003	
	6	700	140	15000		
30363	7	750	200	100	7/29/2003	
	8	750	140	2000		
	9	750	100	15000		
30311	10	800	140	100	8/6/2003	329.9
30343	11	800	100	2000	9/3/2003	
	12	800	80	20000		
30352	13	700	400			

Task 2D: Microstructural Analysis

The objective of the microstructural analysis is to identify the microstructural changes that significantly lead to strengthening, weakening, and internal damage characteristics of each material and to explore how these changes relate to the exposure conditions of the testing.

The University of Cincinnati has undertaken the metallurgical characterization of the USC materials. Techniques for producing foils have been developed, and foils of aged alloy 617 have been examined. A paper for presentation at the TMS meeting is being prepared.

The University has agreed to perform short-time aging and has completed 100 hour aging of samples of CCA617, alloy 230, HR6W, and Super304H stainless steel. Full coverage of temperatures and times are underway at ORNL for the CCA617 and alloy 230. About half of the intended temperatures are in progress for HR6W and Super304H stainless steel. Additional aging furnace capacity is being installed.

A sample of modified alloy 740 was received and sent for machining test bars.

Task 2E: Assessment of Creep-Fatigue Properties

The objective of the creep-fatigue studies is to develop a database that will lead to practical yet conservative methods to address the issue of creep-fatigue damage in the boiler materials.

The fatigue testing matrix has not been defined, so testing has been delayed until such time as meaningful creep-fatigue tests are defined. The need to produce greater creep damage in the creep-fatigue cycle is a major issue that needs to be resolved.

Task 2F: Modeling of Weld Joints

The objective of Task 2F is to produce the experimental data needed model dissimilar metal and thick-section weld joints.

Cross-weld stress-rupture testing of samples from alloy 230 tubes specimens are in progress, as indicated in the table above. All weld, longitudinal weldment, and cross weld specimens are being prepared from plates supplied by Task 5.

Furnaces for testing full thickness weldments have been received and completion of two testing systems is expected in the next quarter.

Task 2G: Study of Accelerated Testing Methods

The objective of the accelerated testing is to provide a method to rapidly characterize changes in the strength of the candidate materials.

Check-out relaxation testing has been completed.

Task 2H: Model Validation

The objective of the model validation testing is to produce a database that can be used to confirm or validate the design rules that are developed in Task 8.

A Skutt furnace has been installed for testing tube bends under pressure. The components for temperature control and data readout have been received.

Electro-hydraulic equipment in the structures test laboratory is now operational.

Designs for deeply-notched test bars have been completed.

Task 3
Steamside Oxidation
(B&W)

Task 3A: Autoclave Testing

Background

Steamside oxidation tests will be performed on commercially available and developmental materials at temperatures between 650°C and 900°C (1202°F - 1652°F).

Experimental

During this quarter, the first two exposures at 650°C (1202°F) were completed. The first exposure had a duration of 904.6 hours, the second exposure had a duration of 1008 hours. A discussion of the experimental procedures and results from the first exposure are presented below. The second exposure was completed at the end of the quarter, so no evaluation results are available at this time.

First Exposure at 650°C (1202°F)

The following is excerpted from a technical paper that will be presented on the results from the first 650°C exposure. This paper, entitled “Preliminary Results From Steam Oxidation Tests Performed On Candidate Materials For Ultrasupercritical Boilers”, will be presented at the EPRI International Conference on Materials and Corrosion Experience for Fossil Power Plants in Charleston, SC on November 18-21, 2003.

Experimental

The first 650°C (1202°F) steam oxidation exposure was performed on 127 specimens fabricated from ferritic steels, austenitic stainless steels, nickel-based alloys and coated materials. The chemical composition of the tested materials is displayed in Table 1. The specimens were hung from an Alloy 601 test frame shown in Figure 1. The first exposure lasted for 904.6 hours. The temperature variations within the retort were continuously monitored, so the test temperature for each specimen was known with certainty. The temperatures within the retort were very stable during the exposure with a maximum standard deviation of <2°C. At the conclusion of the first exposure, 39 of the specimens were removed from the test rack and weighed. Eighteen of these specimens were descaled and re-weighed, 19 of the specimens were cross sectioned and evaluated by SEM/EDX, and 2 specimens were returned to another consortium member (Alstom) for analysis.

The SEM/EDX analyses were performed at Surface Science Western (SSW). The tested coupons were sectioned, mounted and polished to a 0.25μm finish. SEM/EDX analyses were performed on the mounted coupons using a Leo 440 SEM (20 keV electron beam). The SEM was equipped with a Gresham light element detector and a

Quartz Xone energy dispersive X-ray (EDX) analysis system. Secondary electron micrographs were obtained at three different magnifications and the EDX analyses were performed at selected locations of interest. In addition, elemental distribution maps were also collected from a representative region.

Results

Visual observations following the first exposure at 650°C (1202°F) indicated the following:

- Ferritic materials exhibited a gray scale except for the MARB2 material which appeared dull silver.
- Austenitic and nickel-based materials exhibited a dark gray scale.
- Coated specimens exhibited scales that ranged in color form gray to green to silver.
- Exfoliation was observed on T23, P91, P92 and Cereblak-coated P92 specimens.

Oxidation rates and corrosion rates calculated from pre-test, post-test and descaled weight measurements are displayed for the specimens in Table 2. The oxidation rates express the amount of weight change experienced by the specimens during the exposure. Since oxygen is incorporated in the formation of oxides, the specimens typically gain weight; however, factors such as exfoliation and dissolution will reduce the amount of weight gain experienced by a specimen. The oxidation rates were calculated assuming linear kinetics for all materials since test data is currently available after only one time interval. The corrosion rate describes the rate of cross sectional metal thickness loss due to oxidation, exfoliation and dissolution. The results from the SEM/EDX evaluation of the specimens are also contained in Table 2. Selected SEM photmicrographs are displayed in Figures 2 through 5.

Discussion

The preliminary test results at 650°C clearly demonstrate the overriding effect of chromium concentration on the oxidation behavior of the materials. Figure 6 shows a plot of corrosion rate and oxide thickness as a function of chromium content constructed from the data contained in Table 2. This plot shows that the oxidation behavior of materials with less than ~18% Cr is strongly influenced by the Cr content, while the effect of Cr content on oxidation behavior is much less for materials containing >18% Cr. Oxide morphology and composition is also strongly influenced by the alloy chromium content (compare Figures 2 and 5). Figure 6 is in general agreement with a plot generated by Otsuka [1] showing that the oxide thickness formed in 700°C steam increases as the chromium content of the alloys decreases below ~20% Cr.

The one exception to the Cr concentration effect was the 9%Cr MARB2 alloy, which displayed oxidation behavior equal to materials containing ~18%Cr. From the SEM/EDX analyses, the most obvious difference between the MARB2 alloy and the remaining ferritic materials was the presence of significant Cr in the outer oxide layer

(Figure 4). As shown in Table 1, the MARB2 material contained a very high Si concentration (0.73%). Si has been previously reported as being very effective in improving the steam oxidation resistance of ferritic steels [2-4], but Si concentrations above ~0.4% are detrimental to the high temperature creep properties and toughness of ferritic materials [2]. However, along with the high Si level, the MARB2 alloy also contains 3.3% Co, which has been reported to improve creep strength [5]. The thin oxide and low descaled corrosion rate observed with the MARB2 alloy suggest that it quickly formed a protective, chromium-rich oxide that limited further oxidation of this material.

The P92 material seems to exhibit behavior between P91 and the MARB2 alloy. At some locations on the P92 surface, only a single, thin outer oxide was observed, while adjacent locations exhibited thick outer and inner oxide layers (Figure 3). Ferritic materials T23 (2.09%Cr), P91 (8.29%Cr) and SAVE 12 (9.25%Cr) displayed signs of oxide disbonding, while the MARB2 alloy (9.16%Cr) and P92 (8.93%Cr) did not display oxide disbonding.

The results from the current program are in agreement with previous steam oxidation test results, though the oxidation (mass change and oxide thickness) experienced by the materials in the current program are somewhat less than previously reported results. Knödler and Ennis [6] found that Alloy ST22 (equivalent to T23) gained ~40 mg/cm^2 after 1000 hours in 650°C steam, while a mass gain of ~26 mg/cm^2 was observed after ~905 hours in the current program. Literature values for the mass gain of P91 ranged from 6 to 13 mg/cm^2 after 1000 hours in 650°C steam [7,8], compared to ~3 mg/cm^2 in the current program. Mass gains of 15-18 mg/cm^2 from 650°C, 1000 hour exposures of P92 in steam were reported in literature [6,7,9], compared to ~7 mg/cm^2 in the current program. Lapingle [10] reported descaled weight losses of materials following 1000 hour exposures in 650°C steam. He reported weight losses of ~250 mg/cm^2 for T23, ~30 mg/cm^2 for T91, and ~35 mg/cm^2 for T92. Weight losses of ~107 mg/cm^2 for T23, 35 mg/cm^2 for P91 and 13 mg/cm^2 for P92 were observed in the current program.

The parabolic oxidation rate equations derived by Wright [11] from steam oxidation test data predict mass changes of ~59 mg/cm^2 for ferritic steels containing 0-2%Cr, and ~16 mg/cm^2 for ferritic steels containing 9-12%Cr for materials exposed for ~905 hours at 650°C. As with the other literature data presented above, these predicted values are ~2-5 times more than the values that were actually measured during the current test.

The above trend seems to also extend to the austenitic alloys tested. Zabelt [12] reported an oxide thickness of ~20μm for Super 304H exposed to 650°C steam for 1000 hours, while an oxide thickness of ~2μm was observed in the current program. Pearl [13] reported a weight loss of ~1.2 mg/cm^2 for Alloy 625 exposed for 1000 hours in steam at 590-710°C, compared to weight losses of 0.1-0.5 mg/cm^2 for similar alloys in the current program.

The main source of the differences observed between the current test results and other steam oxidation results reported in the literature is probably due to experimental variations. Where descriptions of the specific test environments exist in the literature, it appears that the steam oxidation tests were performed in steam produced from high purity water. Most, if not all, of the tests cited above used water that contained oxygen levels that were much lower than those employed in the current program (100-300 ppb). The tests described in the literature also make no mention of chemical additions to increase the pH of the test solution, as was done in the current program (pH = 8.0-8.5). The steam velocities employed in the other steam oxidation tests ranged from stagnant to 5 liters/sec (compared to 8 ml/min in the current program). It appears that flow did not have a significant impact on the test results. Thus, it is possible that the experimental procedures employed in the current program, designed to simulate the chemistry that is actually used in an operating boiler, may have produced denser oxides that reduced the oxidation experienced by the materials in the current test as compared to literature oxidation results. Since the trends exhibited by materials in the current are consistent with the trends observed in the literature, test temperature and alloy composition remain the most important factors that influence the test results.

The EDX results reveal that nearly all of the materials displayed a zone of matrix Cr depletion below chromium-containing oxide layers, as shown in Figure 5. The oxides on nearly all of the austenitic alloys displayed Mn enrichment and contained levels of Ni and Fe that were significantly below matrix concentration levels.

The chromized P92 specimens performed comparably to the austenitic alloys after the 1,000 hour exposure at 650°C. The post-test cross-section of AlCrP92 specimen (shown in Figure 7) displays an aluminum oxide surface layer above a 15μm layer of slightly Al-enriched matrix composition. Below this layer, a ~15μm Cr-enriched layer was observed, and below this layer was a nearly continuous string of aluminum oxide particles. The electroless Ni material exhibited iron oxide and chromium oxide layers above the nickel plating, indicating that the nickel plating was only marginally successful in limiting oxidation of the base alloy. The Cereblak coating also proved ineffective in significantly reducing the oxidation behavior of the P92 base material.

Conclusions

1. The steam oxidation behavior of the materials tested to-date is predominantly controlled by the alloy chromium concentration.
2. A non-commercial 9Cr ferritic steel (MARB2) containing a high Si concentration exhibited oxidation behavior that was comparable to austenitic stainless steels following steam oxidation for 1000 hours at 650°C. Unlike the other 9%Cr materials tested, a chromium oxide film formed on the surface of the MARB2 base metal during the exposure.
3. Mass change and oxide thickness measurements from the current program were 2-5 times less than literature values reported for comparable materials, temperature and time. Environmental differences between the current program and other programs may have produced the observed differences in oxidation behavior.

4. Chromized coatings on P92 exhibited better oxidation behavior than electroless nickel plated P92 or Cereblak coated P92. Chromized P92 coupons had better oxidation resistance than ferritic steels, but less resistance than austenitic alloys.

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Table 1: Chemical Composition of Test Materials

CHEMICAL COMPOSITION OF TEST MATERIALS												
Material	C	Si	Mn	Fe	Cr	Ni	Mo	W	V	Nb	N	Other
T23	**0.070**	**0.24**	**0.49**	**Bal**	**2.09**	**0.13**	**0.17**	**1.7**	**0.221**	**0.031**	**0.008**	**0.002 B**
P91	**0.11**	**0.37**	**0.48**	**Bal**	**8.29**	**0.14**	**1.03**	**0.024**	**0.22**	**0.068**		**0.18 Cu**
P92	**0.11**	**0.21**	**0.43**	**Bal**	**8.93**	**0.12**	**0.49**	**1.65**	**0.19**	**0.05**	**0.055**	**0.005 B**
MARB2	**0.082**	**0.73**	**0.49**	**Bal**	**9.16**		**<0.01**	**2.47**	**0.2**	**0.048**	**0.0015**	**3.3 Co, 0.019 B**
SAVE 12	**0.12**	**0.28**	**0.54**	**Bal**	**9.25**			**2.92**	**0.30**	**0.05**	**0.01**	**<0.1Nd, 2.68Co**
304H	**0.050**	**0.45**	**1.80**	**Bal**	**18.83**	**11.0**						
Super 304H	**0.080**	**0.25**	**0.45**	**Bal**	**19.10**	**9.57**	**0.15**		**0.064**	**0.50**	**0.096**	**2.73 Cu, 0.11 Co**
Alloy 800HT	**0.070**	**0.27**	**0.76**	**Bal**	**19.49**	**32.32**						**0.56Ti, 0.53Al**
Nimonic 263	**0.050**	**0.07**	**0.33**	**0.34**	**20.02**	**51.17**	**5.91**					**19.51 Co, 2.16 Ti, 0.44 Al**
CCA617	**0.059**	**0.17**	**0.08**	**0.87**	**21.73**	**55.0**	**8.71**	**0.26**	**0.01**	**0.03**	**0.022**	**11.57Co, 1.23Al, 0.41Ti**
SAVE 25	**0.074**	**0.24**	**0.66**	**51.25**	**21.85**	**19.25**	**0.12**	**1.35**	**0.069**		**0.19**	**4.1Cu**
Alloy 230	**0.110**	**0.39**	**0.59**	**1.25**	**22.42**	**Bal**	**1.31**	**14.27**	**<0.05**	**0.05**		**0.22 Co, 0.33 Al, 0.016 La, 0.002 B.**
HR6W	**0.07**	**0.26**	**1.00**	**Bal**	**23.44**	**44.70**		**6.0**		**0.25**		**0.12Ti**
Alloy 740	**0.034**	**0.45**	**0.27**	**1.02**	**24.31**	**49.45**	**0.520**			**1.830**		**0.75 Al, 19.63 Co, 1.58Ti**
HR-120	**0.06**	**0.59**	**0.69**	**Bal**	**25.94**	**36.49**	**0.38**	**<0.1**		**0.66**	**0.23**	**0.05Al, 0.14 Co**

Table 2: Results from 650°C Test – 905 hr Exposure

Material	Average Weight Change per Unit Area (mg/cm^2)	Average Oxidation Rate (g/cm^{2}sec)	Descaled Corrosion Rate (mpy)	Oxide Thickness (microns)	Oxide Composition
T23	25.79	3.30E-10	51.77	150 outer - 50 next - 20 next - 20 inner - 60	outer 2 layers - Fe oxide inner 2 layers - Fe oxide sl. enriched in Si, V & Cr
P91	3.02	3.87E-11	17.4	30 outer - 15 inner - 15	outer - Fe oxide inner - Fe/Cr oxide sl. enriched in Si
P92	7.08	9.06E-11	6.67	5-30 outer - 5-15 inner - 0-15	outer - Fe oxide inner - Fe/Cr oxide highly enriched in Cr and sl. enriched in Si
MARB2	0.34	4.34E-12	0.22	3 outer - 1.5 inner - 1.5	outer - Fe/Cr oxide inner - Cr/Fe oxide enriched in Mn & Si
SAVE12	4.36	5.58E-11	6.75	45 outer - 25 mid - 1 inner - 19	outer - Fe oxide mid - Cr/Fe oxide sl. enriched in W inner - Fe/Cr oxide enriched in Co
304H	0.24	3.07E-12	0.27	5 max	Cr oxide
Super 304H	0.11	1.37E-12	0.2	2	Cr oxide
800HT	0.27	3.44E-12	0.28	2	Cr oxide
Nimonic 263	0.14	1.79E-12	0.09	1 max	Cr oxide
CCA617	0.12	1.50E-12	0.1	1	Cr oxide
SAVE25	0.14	1.79E-12	0.2	1	Cr oxide
Alloy 230	0.21	2.66E-12	0.24	1	Cr oxide
HR6W	0.23	2.93E-12	0.22	<1	Cr oxide
Alloy 740	0.13	1.67E-12	0.09	<1	Cr oxide
HR120	0.20	2.53E-12	0.21	1	Cr oxide
CrP92	0.35	4.53E-12	0.82	up to 10	Cr oxide
SiCrP92	0.39	4.98E-12	0.98	0	N/A
AlCrP92	1.04	1.33E-11	0.17	3	Al oxide
ElessNiP92	1.68	2.15E-11		8 outer - 7 inner - 1	outer - Fe oxide inner - Cr oxide
CBP92	3.95	5.05E-11	Analysis Results Not Available		

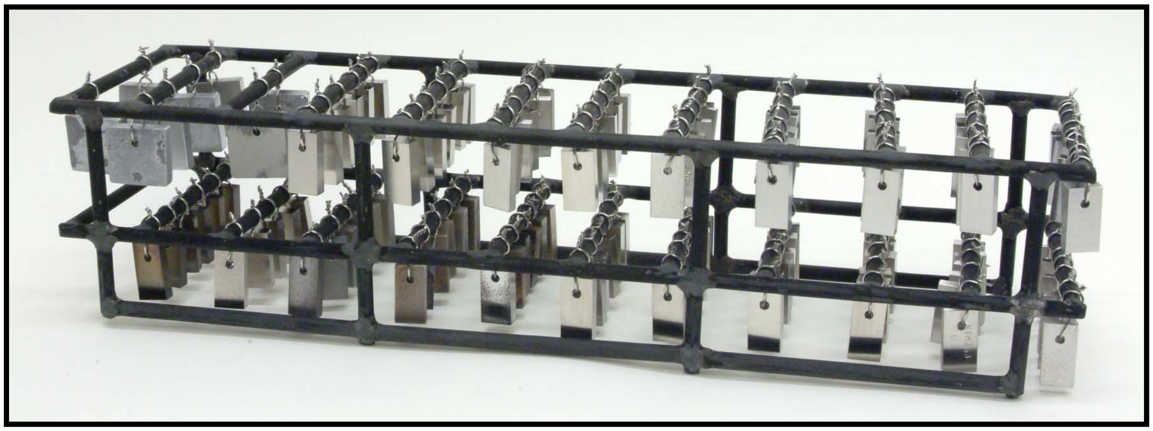


Figure 1. Test Rack and Specimens

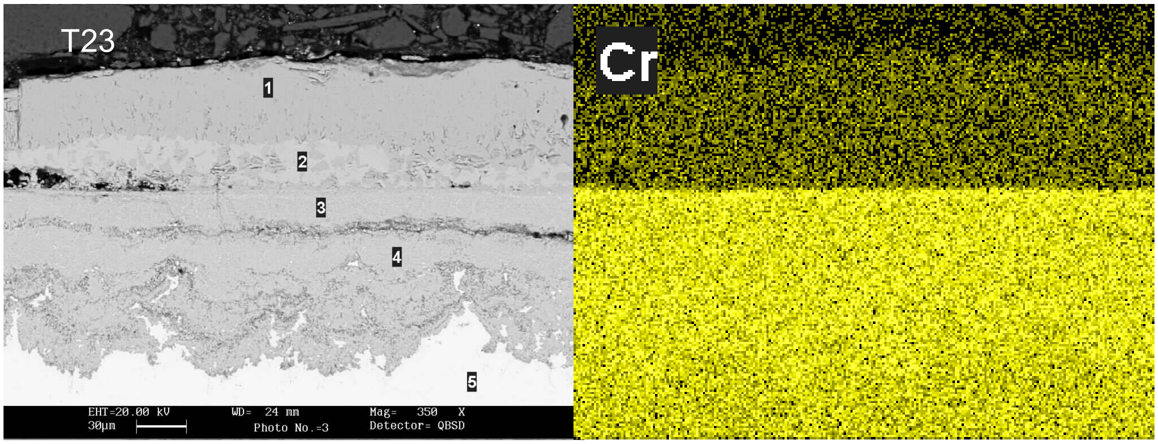


Figure 2. SEM Image and EDX Cr Map for T23 (650°C Steam, 905 hrs)

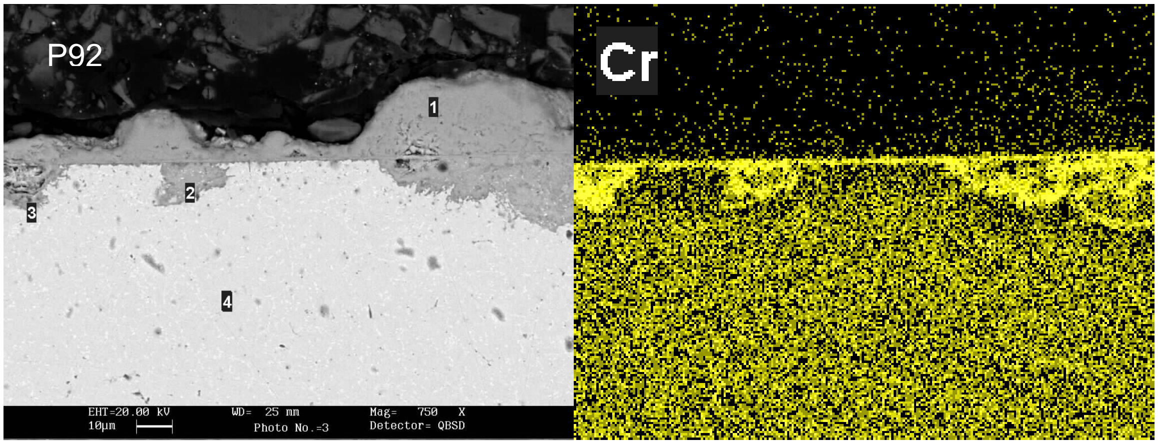


Figure 3. SEM Image and EDX Cr Map for P92 (650°C Steam, 905 hrs)

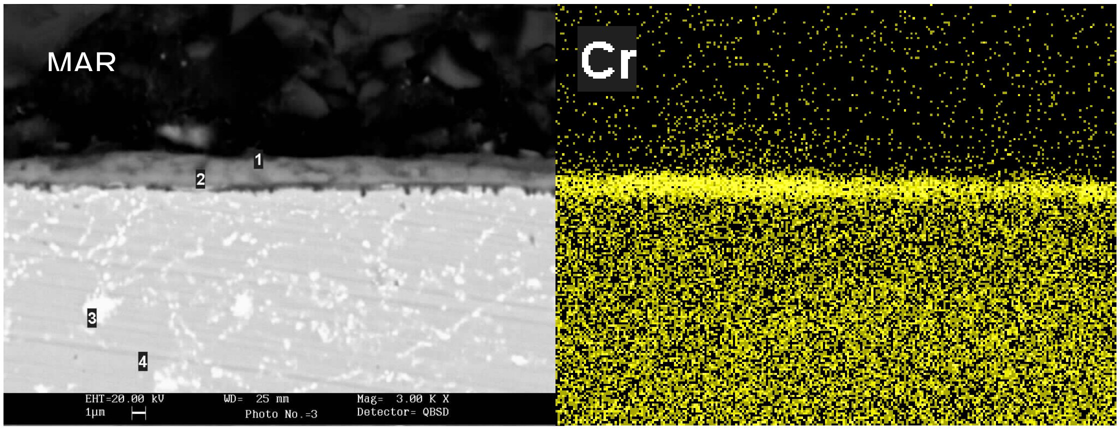


Figure 4. SEM Image and EDX Cr Map for MARB2 (650°C Steam, 905 hrs)

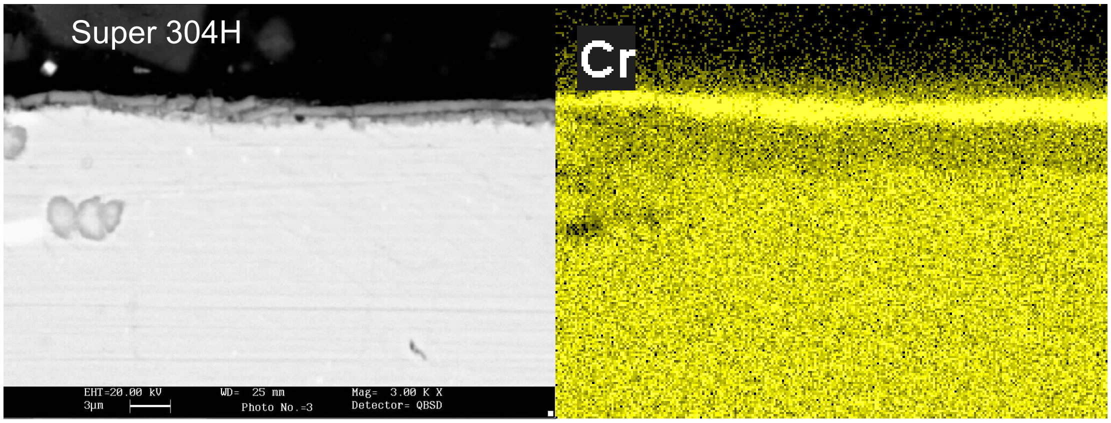


Figure 5. SEM Image and EDX Cr Map for Super 304H (650°C Steam, 905 hrs)

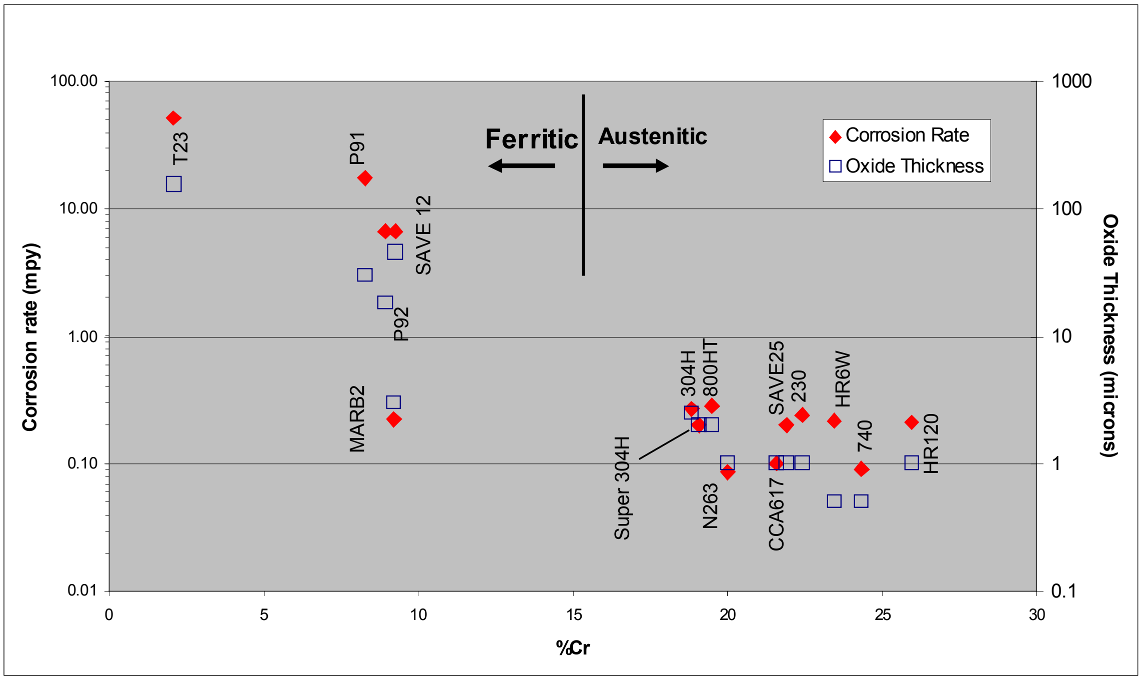


Figure 6. Corrosion Rate and Oxide Thickness as a Function of %Cr (650°C Steam, 905 hrs)

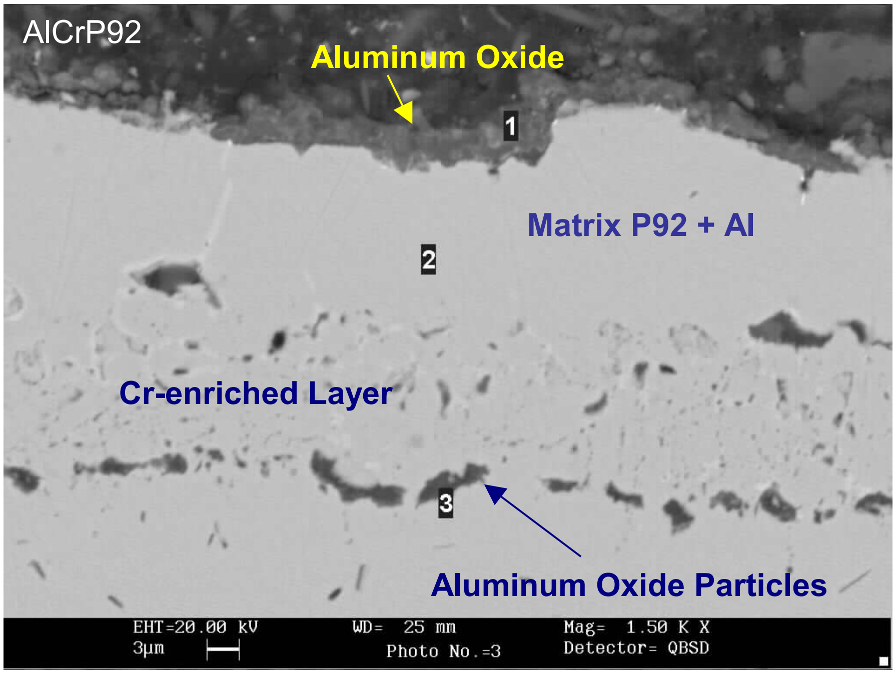


Figure 7. SEM Image of AlCrP92 (650°C Steam, 905 hrs)

Concerns

There are no concerns at this time

Activities Next Quarter

The coupons removed following the second 650°C exposure will be evaluated. From these results, information regarding oxidation kinetics should begin to emerge. The third and final exposure at 650°C will begin early in the first quarter of GFY04 and should conclude early in the second quarter of GFY04 (January 2004).

Task 3B Coating Tests

Background

Coated specimens for steamside oxidation testing will be prepared in conjunction with Task 7 and evaluated after testing.

Experimental

All of the coated specimens that were provided are currently being exposed in the 650°C Steamside Oxidation Test. Results from the first specimens that were removed were discussed in Task 3A above. Thus far, the chromized P92 specimens (Cr, SiCr and AlCr) are exhibiting oxidation behavior similar to that exhibited by other austenitic alloys. The electroless Ni coating on the P92 specimen did not appear to effectively limit diffusion of iron, as evidenced by the iron oxide formed on the surface of the specimen (shown in Figure 8 below).

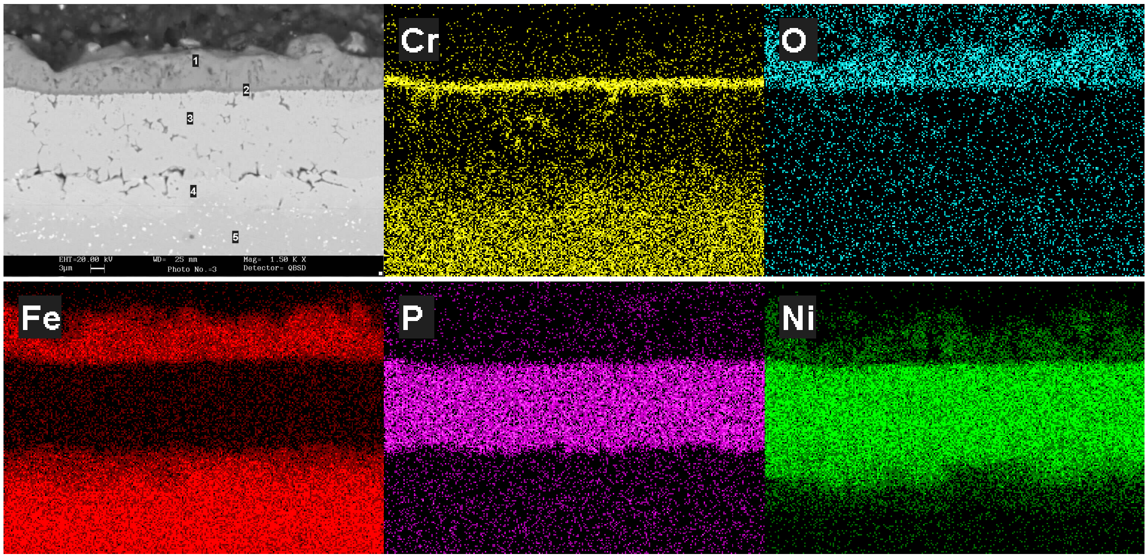


Figure 8. SEM Image and EDX Maps for Electroless Ni on P92 (650°C Steam, 905 hrs)

The Cereblak coated specimens that were exposed during the first 650°C test were sent to Alstom for evaluation. The results from their evaluation have not yet been received by BWRC.

Concerns

There are no concerns at this time

Activities Next Quarter

The coated materials will be weighed and metallographically evaluated as they are removed from the 650°C test. New coated specimens for the 800°C test will be needed by the end of the next quarter.

Task 3C Assessment of Temperature

Background

Based on the steamside oxidation test results, the practical temperature limits for the materials tested will be determined.

Experimental

No progress will be possible until results from the steamside oxidation tests at different temperatures become available.

Concerns

There are no concerns at this time

Activities Next Quarter

None.

Task 3D Review of Available Information & Reporting

Background

Available steamside oxidation literature pertaining to materials and environmental conditions of interest will be reviewed. Project status updates will be prepared and status meetings will be attended as required.

Experimental

The Literature Review was finalized and issued.

Monthly status reports were prepared for July, August and September, 2003, and a Quarterly Report was prepared for the April-June, 2003 time period.

Concerns

There are no concerns at this time.

Activities Next Quarter

Monthly status reports will be written for October, November and December, 2003.

The paper for the EPRI Conference in November in Charleston, SC will be completed and presented.

Task 3E Conduct Experimental Exposures

Background

The steam oxidation behavior of model Fe-Cr alloys will be evaluated.

Experimental

B&W is remaining cognizant of the ORNL tests on these model alloys.

Concerns

There are no concerns at this time

Activities Next Quarter

B&W will maintain cognizance of ORNL activities pertaining to model alloy test results.

Task 3F Characterization

Background

Samples of the model Fe-Cr alloys fabricated in Task 3E will be characterized before and after steamside oxidation testing using metallographic and electron optic techniques.

Experimental

None.

Concerns

There are no concerns at this time

Activities Next Quarter

B&W will maintain cognizance of ORNL activities pertaining to model alloy characterization.

Task 3G Data Analysis and Coordination

Background

The steamside oxidation results will be evaluated to determine the effects of material properties and environmental factors on oxidation behavior.

Experimental

No progress will be possible until the steamside oxidation tests have been completed (GFY2006).

Concerns

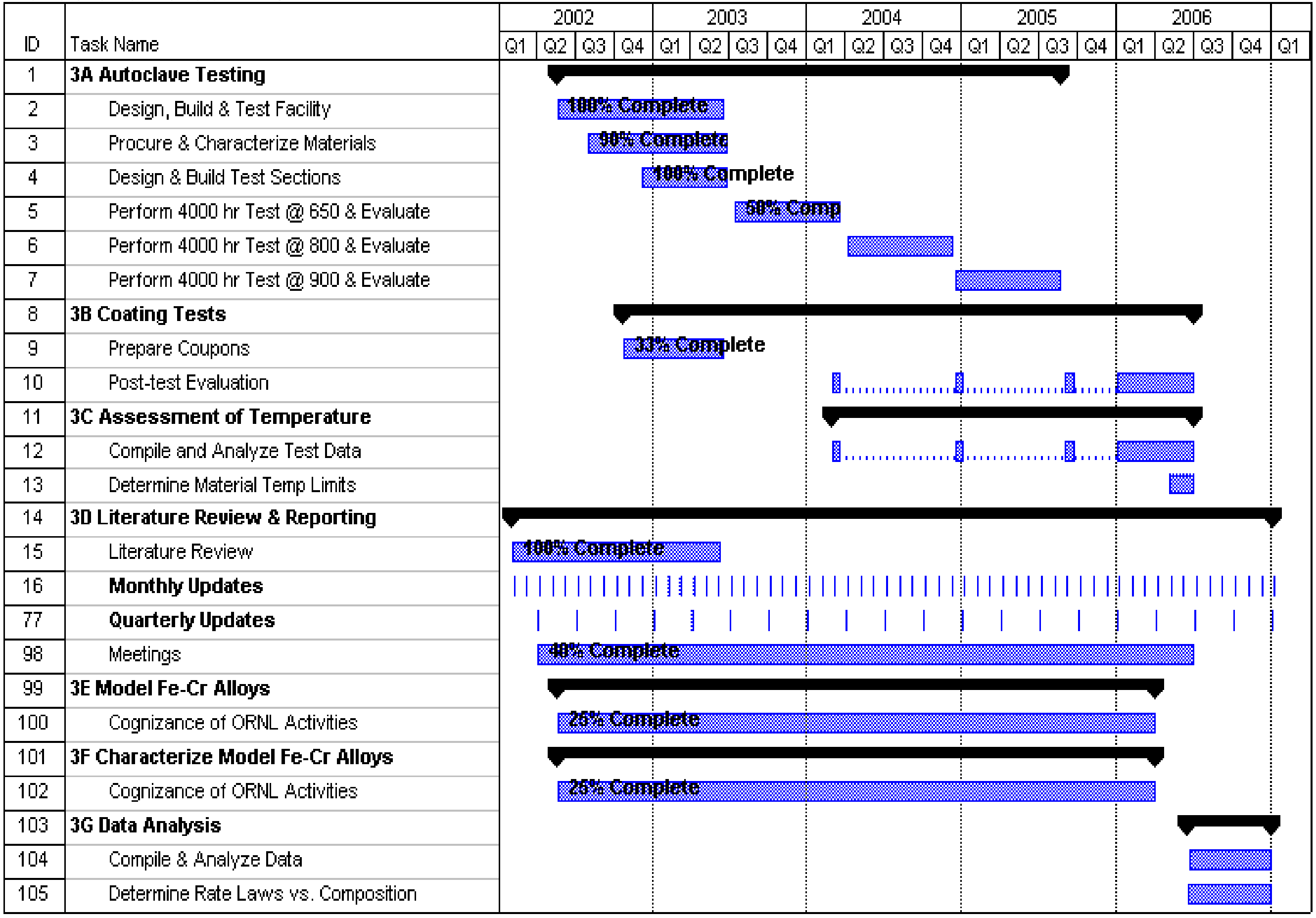
There are no concerns at this time

Activities Next Quarter

None.

Milestone Chart

Dates are listed in GFY



ID	Task Name
1	**3A Autoclave Testing**
2	Design, Build & Test Facility
3	Procure & Characterize Materials
4	Design & Build Test Sections
5	Perform 4000 hr Test @ 650 & Evaluate
6	Perform 4000 hr Test @ 800 & Evaluate
7	Perform 4000 hr Test @ 900 & Evaluate
8	**3B Coating Tests**
9	Prepare Coupons
10	Post-test Evaluation
11	**3C Assessment of Temperature**
12	Compile and Analyze Test Data
13	Determine Material Temp Limits
14	**3D Literature Review & Reporting**
15	Literature Review
16	**Monthly Updates**
77	**Quarterly Updates**
98	Meetings
99	**3E Model Fe-Cr Alloys**
100	Cognizance of ORNL Activities
101	**3F Characterize Model Fe-Cr Alloys**
102	Cognizance of ORNL Activities
103	**3G Data Analysis**
104	Compile & Analyze Data
105	Determine Rate Laws vs. Composition

Task 4
Fireside Corrosion
(Foster Wheeler)

The objective of the task is to evaluate the relative resistance of various advanced alloys to fireside corrosion over the full temperature range expected for the USC plant

Task 4A: Laboratory Testing

Objectives

To perform laboratory tests on candidate alloys exposed to various deposits representative of the three coals at the range of temperatures expected for the USC plant.

Progress for the Quarter

- The procurement of the test materials has proceeded well with only five materials still presently unaccounted for (T23, 347HFG, Nimonic 263, NF709, and HCM12A). A contact with the one material manufacturer has agreed to provide us with four of the five missing materials. The materials already in-house have been identified/characterized and are ready for testing.
- The final modifications and checks of the testing retorts and flue-gas blending equipment have been successfully completed. The final system-wide shakedown will be performed shortly upon the receipt and installation of the proper furnace controllers.
- The composition of the WW test deposits and flue gases is also close to being finalized. Research is still being performed to determine suitable deposit and gas compositions for the SH section of the project.

Concerns

- Procuring the missing materials need to round out the materials testing roster.
- Defining/testing WW deposits and flue gas compositions that are a good representation of what is observed in the field.
- Defining/testing SH deposits and flue gas compositions that are a good representation of what is observed in the field.

Plans for the Next Quarter

- Complete the procurement of the missing materials.

- Finalize WW and SH deposits and gas compositions and begin 100-hour preliminary testing.

Task 4B: Corrosion Probe Testing in Utility Boilers

Objectives

To install corrosion probes of various alloys at three coal-fired power plants and control them at the temperature ranges expected for the USC plant.

Progress for the Quarter

- Development work has begun on various probe retraction mechanisms. In addition, the instrumentation and control needs of the probes have also been reviewed with previous corrosion probe designs being used as a template.
- Software and hardware enhancements for the DAQ/control system have been finalized and will soon be ordered.
- With respect to the host utilities, the host proposal document was prepared, reviewed, and sent out to prospective host utilities. The utilities that are showing interest are Xcelenergy, TVA, FirstEnergy, AEP, and CINERGY. Presentations were made at FirstEnergy's Burger Station and Xcelenergy's Pawnee Station. Both appear willing to participate as host sites. CINERGY has recently shown some interest in participating in the program at their Gibson Station.

Concerns

- Developing a viable retraction mechanism to accommodate the longer probe design/weight.
- Finalizing the 3 host utilities for the program.

Plans for the Next Quarter

- To secure the 3 host utilities.
- Finalize probe design.

Task 4C: Steam Loop Design, Construction, and Testing (B&W and Riley Power)

Objectives

- The objectives of this subtask are to design, build, and test two experimental USC steam loops that will operate in a commercial boiler at metal temperatures up to 1400ºF. The elements of this subtask include the following:

- Design and construct two test loops using commercially available, high temperature corrosion resistant alloys selected for the USC Boiler Development Project.
- Install and operate the test loops at the Reliant Electric power plant, located in Niles, OH and burning high sulfur Ohio coal, and at another utility.
- Test and monitor the relative performance of the USC tube alloys, coatings, claddings, and welds which comprise the test loops for a period of 24 months.

Progress for the Quarter

With regard to the test loop at the Reliant Plant:

- The test section loops were completed and successfully hydro tested at B&W's Research Center and signed off by the Authorized Inspector.
- All erection and arrangement drawings were finalized and released.
- Reducers that connect the test section loops to the existing inlet tubing and to the attemperator were welded and sent out for x-ray, and the completed loop was transported to the plant.
- On-site meetings were held with various contractors needed for installation of the test loops.

With regard to the second test loop:

- The Mt. Tom host site was rejected by the steering committee because it was burning imported coals primarily from China and South America.
- The search continues for a host site burning PRB coal.
- Dairyland Power Cooperative was contacted in September.

Concerns

- No concerns for the installation at the Reliant Plant.
- Need to finalize a second host site.

Activities Planned for Next Month

- Take all materials to Reliant site for installation of test loops.
- Oversee and complete installation.
- Continue discussions with Dairyland Power Cooperative as a potential host site.

Task 5
Welding Development
(Alstom)

The major objectives for Task 5: Welding Development are:

- To define weld metal choices for candidate materials.
- To establish acceptable welding procedures and practices.
- To evaluate the effects of manufacturing heat treatments and preheat and post weld heat treatments on weldment integrity and properties.
- To produce samples needed to determine the properties of candidate ultrasupercritical alloy welds and weldments, including the dissimilar metal weld joint between the various types of material (the actual mechanical and property testing will be performed under Task 2).

These objectives will be accomplished through execution of five sub-tasks. Where activity on these sub-tasks occurred during the reporting period, it is described below.

Task 5A: Selection of Weld Filler Material

Objectives

The primary objective of this subtask is to select and procure appropriate filler materials for each of the welding processes to be studied. However, procurement of base materials and general planning of task activities are also included.

Progress for the Quarter

- The distribution of HR6W tubing and SAVE 12 pipe to other consortium members was completed.
- The plan for welding studies using the HR6W and SAVE12 materials has been finalized and approved by the Riley Power Inc. Manufacturing facility located in Erie, PA. This plan includes the selection of weld filler materials, the optimization of the welding procedures, preparation of sample material for laboratory testing, weldability testing, and the examination of dissimilar metal welds. The welding tests for the HR6W and SAVE12 materials are presently scheduled for November and December 2003.

Concerns

The following concerns have been expressed before and are not new.

- Base material sourcing difficulties and long delivery times have, in some cases, delayed the start of welding activities by 9 to 12 months.
- The unexpectedly high cost of the nickel base alloys will cause the material budgets to be exceeded and might result in program cost overruns and/or reductions in program scope.
- Delivery of Inconel 740 weld wire continues to be a problem. Special Metals is attempting to find the material that was lost during shipping, but the welding development schedules are slipping.

Plans for the Next Quarter

Complete procurement of filler metal for HR6W and SAVE12 materials.

Task 5B: Optimization of Weld Parameters

Objective

The primary objective of this subtask is to establish the baseline welding parameter values for each material/process/product form combination being studied. Included is the development of preheat and post weld heat treatment requirements.

Progress for the Quarter

- **Super 304H**
  Attempts to weld Super 304H tubing using an automatic gas metal arc process were unsuccessful because the filler metal would not wet and tie into the base material, even with adjustments to travel speed and gas mixture. Assistance was being sought from Sumitomo, the material supplier, and from other organizations that might have had experience welding this material with a gas metal arc process, but these efforts have been fruitless. Plans are now being made to try to solve the problems completely within Alstom.

  An orbital gas tungsten arc process was qualified for making tube butt joints and samples are being prepared for mechanical property characterization by Oak Ridge.

- **CCA 617 (known in Europe as Marcko)**
  Attempts to weld CCA 617 plate using a shielded metal arc welding process were unsuccessful because of poor weldability exhibited by the CCA 617 electrodes. Conventional Inconel 617 electrodes, which were procured and tested, had good weldability and did not exhibit the slag control problems that plagued the CCA 617 filler material. The electrode supplier is still investigating this problem, but, if a solution is not identified, current plans are to weld test plates using conventional

Inconel 617 and CCA 617 fillers, the latter on a “best effort” basis, and then compare the properties of both weldments. This would help determine if the matching filler is required for welding CCA 617 plate or if the conventional material is adequate.

The wire feed problems encountered while trying to make tube butt joints using an orbital gas tungsten arc process have been solved and this process was qualified. Samples are now being prepared for mechanical property characterization by Oak Ridge.

A submerged arc process for welding the plate material has been developed and qualified and samples are being prepared for mechanical property characterization by Oak Ridge.

- **Haynes 230**
  Development work to join thick plates using a gas metal arc process was completed and a procedure qualification plate is being prepared as the next step.

- **Inconel 740**
  The Task 5 activities were affected by the work required to complete the Niles test loop, but, now that this loop is complete, Task 5 efforts will increase during the next quarter.

  Welding development on Inconel 740 has been hindered by the lack of filler wire. Even an attempt by Special Metals to deliver the material was thwarted when the shipment was lost. Attempts to find the filler are underway.

  A proposal for additional Inconel 740 Weldability studies was submitted to both the OCDO and the DOE. The OCDO approved the project and the DOE is expected to make a decision by early October.

Concerns

- Submerged arc welding, a high deposition rate process favored by boiler makers for thick sections, does not appear feasible for all nickel base materials. Tests on Haynes 230 and Inconel 740 have been unsuccessful because of cracking and the process is being abandoned on these two alloys.

Plans for the Next Quarter

- Weld thin plate Inconel 740 (if wire is available).
- Begin thick plate welding of Haynes 230.
- Begin thick plate welding of Inconel 740.
- Fabricate Super 304H test specimens using gas tungsten arc process.
- Resolve issues with gas metal arc welding of Super 304H.

- Fabricate test specimens using gas tungsten arc process on CCA 617 tubing.
- Resolve issues with shielded metal arc welding of CCA 617 plate.
- Fabricate test specimens using submerged arc process on CCA 617 plate.
- Start welding efforts on HR6W and SAVE 12.

Task 5: Welding Development - Milestone Chart

(DOE Fiscal Year Basis)

(percentages indicate fraction of workscope completed as of 2003Q4)

		Year 2002				Year 2003				Year 2004				Year 2005				Year 2006			
Task	**Milestone**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
5A	Selection of Weld Filler Material																				
	• Procure base metal for weld trials.	△					100%	▲													
	• Evaluation and selection of filler.	△					90%			▲											
	• Procurement of candidate fillers.	△					70%			▲											
5B	Optimization of Welding Parameters																				
	• Preliminary weld trials and parameter optimization – thin section.				△		40%					▲									
	• Preliminary weld trials and parameter optimization – thick section.				△		30%					▲									
5C	Preparation of Laboratory Samples																				
	• Material preparation.					△		15%					▲								
	• Sample fabrication.						△	10%					▲								
5D	Weldability Testing						0%	△						▲							
5E	Examination of Dissimilar Metal Welds.																				
	• Weld trials						0%				△			▲							
	• Metallurgical analysis						0%					△				▲					
	• Analysis and test case.						0%					△					▲				

Task 6
Fabrication

The objective of Task 6 is to establish boiler fabrication guidelines for the high temperature, corrosion resistant alloys selected for the USC Project. Goals in this effort are:

- To establish fabrication guidelines for the alloys needed to produce USC boiler components.
- To determine the effect of fabrication operations on the properties of USC alloys.
- To determine the thermomechanical treatments or other remedial actions necessary to restore material properties which might degrade due to fabrication operations.
- To investigate prototypical manufacturing operations for producing both thick wall and thin wall components from the USC alloys.

Progress for the Quarter

The efforts towards developing fabricability assessment procedures and operations were continued during task member teleconferences and meetings. Discussions focused on the details of a tapered tube, instead of a bar, that would be used to produce a continuously varying gradient of cold strains to study conditions that cold formed parts would encounter during fabrication and service. The tube configuration would, with a single sample, provide sufficient material for the required studies whereas using multiple bars would require more machining and straining steps. The obvious drawback is that a much higher capacity tensile testing machine would be required thereby limiting the number of facilities available to perform the straining. The tapered tube configuration was adopted and, because Foster Wheeler has a machine capable of straining the full-size tubes, that organization was contracted to perform the machining and straining required for Super 304H and CCA617, the two materials that Alstom is studying. All other efforts associated with the examination of these materials will be performed in the Alstom laboratories.

During this quarter, a Task 6 Committee meeting was held at NETL on July 16th. Progress in Task 6 was reviewed at the USC Steering Committee meeting that was simultaneously held at NETL in Pittsburgh, PA on July 16th and 17th. Also during July, preliminary design concepts for fabricating demonstration superheater and header components were considered and assessed. Fabrication of these components is anticipated to begin at B&W in June, 2004.

On August 4th in response to an EPRI request, B&W gave a presentation entitled, “An Overview of the Ultrasupercritical Materials Development Project,” at the Combustion Technology University Alliance Workshop that was held in Columbus, OH. Also during

August, alloy 230 U-bends produced at the BWC production facility last June were dimensionally characterized and assessed for ovality.

There was a delay this quarter in the fabrication study work of the HR6W and SAVE12 material as proposed in the quarterly report for July 2003. During this quarter, Riley Power Inc. finalized the development plan for the fabricability of HR6W and SAVE12. The Plan, which was submitted to the Task 6 Committee, includes bending tests, PWHT requirements, machining, swaging, drilling, cutting and pressing operations for the above materials. The implementation of this plan and the fabricability testing of the HR6W and SAVE12 material is currently scheduled to take place in November 2003. Riley Power Inc. intends on having Foster Wheeler perform the strain response/recrystallization and precipitation studies on their materials and has issued a purchase order to Foster Wheeler for the performance of the work in October / November 2003.

On September 18th, a Task 6 Committee telephone conference was held to discuss progress against the workscope for Task 6. Also during September, B&W, Alstom, and Riley Power sent samples of 230, HR6W, SAVE 12, CCA617, and Super 304H to Foster Wheeler for conducting the strain response/recrystallization and precipitation studies of these materials under Task 6. Expenditures for Task 6 for work were reviewed by each of the Task 6 participants and compared to original proposed estimates for assessing workscope progress against expenditures and resources, consistent with responsible project management practices.

Concerns

None.

Plans for the Next Quarter

During the next quarter, strained and thermally treated specimens of the six USC alloys (740, 230, CCA617, Super 304H, HR6W, and SAVE 12) will be produced for metallurgical examination and characterization to help assess the fabricability of these materials. Some of this work will be subcontracted to Foster Wheeler by B&W, Riley Power, and Alstom. During the Project Steering Committee meeting planned during November in Columbus, OH, a Task 6 Committee meeting will be held to review workscope plans and progress.

Task 7
Coatings
(Alstom)

The major objectives for Task 7 Coatings are:

- Review state-of-the-art of coating technology and identify development needs.
- Develop coating manufacturing techniques, which can provide corrosion/erosion protection for components in USC boilers, cost effectively.
- Establish manufacturing techniques for application of internal coatings for oxidation protection, cost effectively.
- Provide coated samples for corrosion and oxidation testing in the laboratory and "in the field".
- These objectives will be accomplished through execution of eight sub-tasks. Where activity on these sub-tasks occurred during the reporting period, it is described below.

Task 7B: Coating Feasibility (Internal Coatings)

Objective

The primary objective of this subtask is to examine internal tube coating techniques for oxidation protection.

Progress for the Quarter

- Experimental work aimed at defining new formulations to generate higher Si-containing diffusion layers gave non-reproducible trends. Preliminary work with a Si-F-based activator indicated the coating process to be very fast and difficult to control.

Concerns

No concerns at this time.

Plans for the Next Quarter

Results of tests conducted at lower temperatures will be completed and reported.

Task 7C: Coating Recommendations

Objective

Provide an evaluation of scaleup potential and costs for internal tube coating systems.

Progress for the Quarter

Waiting finalized data from other subtasks.

Concerns

No concerns at this time.

Plans for the Next Quarter

Continue evaluation of ID coating requirements.

Task 7D: Laboratory Testing

Objective

Evaluate corrosion/oxidation response of candidate coating systems.

Progress for the Quarter

Steam oxidation testing using a TGA exposure system continued. Test results for the quarter are detailed in the attached appendix. Planned tests have now been completed. The benefit imparted by these diffusion layers on the susceptibility of T-92 to steam oxidation were documented in a publication presented as part of the Workshop on Scale Growth and Exfoliation in Steam Plant organized by the National Physical Laboratory under the sponsorship of EPRI. A copy of the publication is included as an appendix. Short-term exposures, 100 h, to superheated steam in the temperature range 650 to 750 C demonstrated the superior performance of these layers with oxidation kinetics comparable to that of S304H at 750 C. Different from S304H, no evidence of localized attack was documented for any of the diffusion layers. The results were bench-marked against bare T-92 tested at 650 C.

Concerns

None.

Plans for the Next Quarter

- Review need for any additional steam oxidation tests and execute as necessary. Define additional laboratory testing needs.

Task 7E: Process Scaleup

Objective

Perform coating process trials at an intermediate scale between laboratory and commercial size.

Progress for the Quarter

Part 1: B&W Effort

ASB has been released to develop parameters for depositing 50Ni/50Cr on carbon steel and Haynes 230 tubing. Two deposition processes are being evaluated, HVOF and cold spray. Thin plate samples have been prepared to evaluate a matrix of parameters for both processes. Based on an assessment of these samples, optimum parameters will be selected and used to coat tubes. When this phase is successfully completed, consideration will be given to employing either, or both, processes to deposit MCrAlY coatings on the same substrates.

A meeting has been scheduled with Praxair in early October to discuss their potential involvement in developing samples for assessment using laser surfacing.

Part 2: Alstom Effort

The laboratory work required to define the guidelines for the scaleup test was completed during this quarter. Formulations for the ID coating of tubular components were selected considering the effect of the ID bore size on the pack powder throw-power. The alloys selected for the scale-up tests include S304H and T-92.

The first scale-up test was completed at the end of this quarter. The complete evaluation of results will be reported during the month of October.

Scale-up Tests

The scale-up test will be conducted using tubular components made of S304H and T-92. From 8 to 10 five-ft sections of tubing will be used per test and thermocouples will be attached to each section to monitor the heating cycles through the pack. The components and the pack powder will be assembled in a steel retort that will be sealed with a welded lid with a vent for the gases produced during the decomposition of the activator system. A wall-fired gas furnace will be utilized to conduct the tests. The temperature of the pack will be recorded using an analog reader coupled with a digital converter to store the data in a lap top computer. The description of the formulations for the ID and OD of the tubing pieces is reported in table 1.

Process	ID	OD
Chromizing	30 % Cr 3 % NH4Cl, Bal. Al2O3	43 % Fe-Cr 3 % NH4Cl, Bal. Al2O3
Si-Cr rich layer	3 % Si, 30 % Cr 1 % NH4Cl, 1 % CaF2 Bal. Al2O3	2 % Si, 25 % Cr 1 % NH4Cl, 1 % CaF2 Bal. Al2O3
Al-Cr rich layer	4 % Al, 20 % Cr 2 % NH4Cl, 2 % MgCl2 Bal. Al2O3	2 % Al, 18 % Cr 1 % NH4Cl, 2 % MgCl2 Bal. Al2O3

The S304H tubing has 2.5” OD with 0.35” wall while the T-92 tubing has 1” OD with a 3/16” wall. The OD formulation will used to coat the ID and OD of the S304H tubing but because of the smaller ID of the T-92, the ID formulations have been slightly modified to increase the throw-power of the powder to generate coatings with similar characteristics to that of the OD. The ID of the component determines the amount of powder that can be used. As pre-determined from laboratory tests, an ID of 13/16” requires an increase in the metal constituents of the pack to be able to provide a coating composition similar to that of the OD. The hold time for these tests will be similar to that from laboratory experiments, i.e. 16 hours. Modifications to the test facilities and adjustments to processing parameters will be implemented as needed. The objective of these tests is to define the optimum processing conditions to generate a consistent product. The tests will begin using the chromizing formulation followed by the Si-Cr and Al-Cr rich layers. The matrix will include a limited number of tests where the OD and ID will be coated with different system formulations.

The first scale-up test was conducted using 8 sections of S304H tubing. Thermocouples were position as to obtain a 3D profile of the heating characteristics of the pack. The load of about 1000 pounds of powder took about 29 h to reach the processing temperature. The components toward the walls of the retort reached the processing temperature within 16 h. Modifications to the heat process will be implemented in subsequent runs. The pack powder was a chromizing formulation and the metallographic work will be completed by the second week of October. The quality of the layers will be correlated to the temperature and processing time. Samples will be section according to the placement of the 8 thermocouples. A detail report will be issue at the end of October.

Si-Cr rich Layers

The reduction of Silica by Al-powder is thermodynamically feasible. Al-powder could be used to reduce silica releasing elemental Si that could be combined with the halide activator to be implanted during the diffusion process. Formulations mixing Al powder and replacing part the Alumina filler with silica failed to generate Si-Cr rich layers of the type attainable using the CaF2 based activator system. The systematic substitution of Alumina by Silica only generated chromized layers and those formulations with 6 and 12 wt% Silica were the only ones that resulted in the formation of a Cr-rich layers with about 1 to 2 wt% Si. The target silicon content is between 3 and 5 wt%.

Another approach that was promising based on thermodynamic calculations considered the utilization of a SiF-ammonia base compound to be used as the activator. Minor variations in the composition of the powder resulted in dramatic differences in the diffusion kinetics. A systematic variation with respect to temperature is planned for the month of October. The most promising result consisted of a diffusion layer with as much as 8 wt% Si and a marginal increase in chromium of the order of 16 wt%. The coating-base metal interface was wavy with discrete intergranular porosity, both features indicative of fast kinetics. The process temperature will be decreased in 50 C increments but not lower than 1000 C.

Concerns

None.

Plans for the Next Quarter

- Finalize ASB's evaluation of HVOF and cold spray for coating 50Ni/50Cr on tubing of interest.
- Decide how and whether to further the evaluation of HVOF and/ or cold spray.
- Potentially pursue laser surfacing work at Praxair.
- Completion of the tests designed to evaluate the effect of temperature on the Si-Cr rich layers obtained using a Si-F-ammonia activator.
- Execution of the first T-92 chromizing scale-up test and of the second S304H chromizing test.
- An experimental program designed to evaluate the effect of unburned carbon on the coal-ash corrosion mechanism will be submitted for consideration by the steering committee.

Task 7H: Specimens for Field Corrosion/Oxidation

Objective

Provide externally and internally coated specimens for inclusion in corrosion/oxidation testing under Tasks 3 and 4.

Progress for the Quarter

No activity.

Concerns

None.

Plans for the Next Quarter:

Finalize schedule for coatings test samples for the second steam loop and corrosion probe field exposures.

Task Name	Status
Task 7: Coatings	
Task 7A: Detailed Study of Current State of the Art	
Alstom Task 7A: Detailed Study of Current State of the A	Complete
Task 7B: Coating Feasibility (Internal Coating)	
Alstom Task 7B: Coating Feasibility (Internal Coating)	95%
Task 7C: Coating Recommendations	
Alstom Task 7C: Coating Recommendations	15%
Task 7D: Laboratory Testing	
Alstom Task 7D: Laboratory Testing	50%
Task 7E: Process Scale Up - Preliminary Trials	
Alstom Task 7E: Process Scale Up - Preliminary Trials	40%
B&W Task 7E: Process Scale Up - Preliminary Trials	25%
Task 7F: Process Optimization	
Alstom Task 7F: Process Optimization	
B&W Task 7F: Process Optimization	
Task 7G: Manufacturing Recommendations	
Alstom Task 7G: Manufacturing Recommendations	
B&W Task 7G: Manufacturing Recommendations	
Task 7H: Specimens for Field Corrosion/Oxidation	
Alstom Task 7H: Specimens for Field Corrosion/Oxidatior	40%
B&W Task 7H: Specimens for Field Corrosion/Oxidation	40%
Task 7I: Project Management	
Alstom Task 7I: Project Management	Ongoing
B&W Task 7I: Project Management	Ongoing

Note: Dates refer to DOE fiscal year calendar 10/01/yyyy to 09/30/yyyy+1

Appendix I
Appendix to July-September Quarterly Report
Evaluation of Steam Oxidation Testing

Introduction

Short-term steam oxidation tests by thermogravimetric analysis (TGA) were conducted on various samples of Grade 92, Super 304H, and nickel-base alloys to evaluate coating performance and oxidation resistance at 650°C and 750°C. Following post-test weight gain determinations, samples were examined in cross-section by optical microscopy to characterize the coating or oxidized surface, and by SEM/EDS to determine compositional profiles and the extent of oxidation. Scanning electron micrographs were acquired in the backscattered electron mode. The current report summarizes the findings of the tests performed in this reporting period.

Results

The samples tested and examined for this reporting period include:

1. Grade 92 with Si-Cr layer (750°C)
2. Grade 92 with Al-Cr layer (750°C)
3. Super 304H (750°C)
4. Grade 92 with Cerablak coating, pre-oxidized in air (650°C)
5. CCA 617 (750°C)
6. Haynes 230 (750°C)

Weight Gain

Weight gain results as measured by TGA are presented in Table 1. All but the Cerablak-coated Grade 92 samples tested experienced low weight gains (<1 mg/cm^2).

Per the recommendation of the coating vendor, the Cerablak-coated Grade 92 sample was pre-oxidized in air at 650°C for one hour, and allowed to cool to ambient temperature prior to steam exposure at 650°C. A post-test visual examination showed the surface to be uniformly covered with a reddish-orange oxide. The Cerablak-coated Grade 92 sample exhibited a weight gain of 8.9 mg/cm^2. Recall that a previous test at 650°C with a similar sample that was not pre-oxidized yielded a comparable weight gain of 8.8 mg/cm^2 (See April-June Quarterly 2003 report). While the weight gains were virtually identical, the oxide on the pre-oxidized sample was intact, with no evidence of spallation, while the sample that was not pre-oxidized had a gray exfoliating oxide.

Metallography and SEM/EDS

Grade 92 Si-Cr

Optical and scanning electron micrographs of the Grade 92 Si-Cr surface are shown in Figures 1 and 2, respectively. The irregularly shaped protrusions that covered most of the surface are inherent to the coating, as they also appear in as-received samples. The Si-Cr layer was about 525 µm thick. The EDS analysis results (Table 2) and corresponding concentration profile (Figure 3) shows the highest chromium (~ 35wt.%) and silicon (~ 3 wt.%) levels at 1-10 µm depths. The lowest chromium levels were about 10% near the base metal interface. Only a trace of silicon (0.1%) was detected near the base metal interface.

Grade 92 Al-Cr

The post-test characteristics of the Al-Cr diffusion coating are illustrated in the optical micrograph (Figure 4) and SEM images (Figures 5 and 6). The Al-Cr layer was about 800 µm thick. The micrographs clearly depict an approximately 400 µm thick zone containing aluminum nitride precipitates. Above this zone, at the surface (Area 1), the coating is irregular with a high void density. The light-colored phase (Area 2) near the surface consists primarily of chromium. At a depth of about 40 µm from the original surface is a 10-15 µm thick discontinuity (Area 3) that EDS results show to contain aluminum oxide. This band is also observed in as-received samples and has been found to contain alumina powder from the pack. The concentration profile (Figure 7) shows the highest chromium (~14 wt.%) and aluminum (~8 wt.%) levels in the upper 50 µm of the layer. The post-test characteristics of the coating are identical to those in as-received samples. The only notable distinction between the sample previously tested at 650°C and the one tested at 750°C is the observation of chromium rich particles in the latter sample.

Super 304H

The optical micrograph (Figure 8) shows an overall view of the surface. Higher magnification SEM images of the surface are shown in Figures 9 through 11. Illustrated in Figure 9 is a 1 µm thick oxide at the surface that EDS results suggests to be a chromium-rich spinel. Below this oxide is a 3-4 µm region (Area 2) exhibiting porosity and a different morphology relative to the underlying base metal (see Figure 10). The EDS results indicate this zone approximates the base metal composition. Figure 11 illustrates an area exhibiting localized attack extending approximately 25µm deep . There were only a few of these penetrations over the entire surface of the coupon. The EDS results suggest spinel formation at the surface (Area 1) and within the penetrations (Area 2). A light colored region (Area 3) is shown to be chromium deficient relative to the base metal. Area 4 represents the reference base metal composition. The thin fissures (Area 5) contain a chromium and iron rich oxide with appreciable manganese (~7%). These isolated oxide penetrations are not uncommon in stainless steels. Recall that the sample previously tested at 650°C also exhibited localized attack.

Grade 92 with Cerablak Coating (pre-oxidized)

Optical and scanning electron micrographs of the Cerablak-coated Grade 92 surface are shown in Figures 12 and 13, respectively. A multi-layered oxide is depicted, with a total thickness of about 150 µm. EDS results (Table 2) suggest the 50 µm thick outermost layer to consist of an iron oxide (presumably hematite owing to its brick red color). Beneath the hematite layer is a duplex oxide consisting of magnetite (outer oxide) and an Fe-Cr spinel (inner oxide), each being about 50 µm thick. The metal/oxide interface was chromium enriched. The major distinction between the pre-oxidized sample above and a similar sample previously tested that was not pre-oxidized, was the presence of the hematite layer.

CCA 617

Optical and scanning electron micrographs of the CCA 617 surface are shown in Figures 14 through 16. The surface was uniformly covered with a very thin film (approximately 2-3 µm thick), that EDS results show to be composed primarily of chromium oxide, with a significant level (5%) of silicon. Surface penetrations, extending about 3 µm below the surface were filled with Ni, Cr and Al rich oxides, along with the major alloy additions cobalt and molybdenum.

Haynes 230

The optical micrographs (Figures 17,18) show overall views of the very thin oxide film that uniformly covered the surface. The high magnification SEM image of the surface (Figure 19) shows the oxide to be about 1 µm thick (with some shallow oxide penetration) that EDS results suggests to be a chromium oxide. Area 2 represents the reference base metal composition.

Conclusions

- The silicon- chromium diffusion coating on Grade 92 material provided excellent short-term steam oxidation resistance in 750°C test environments. The Al-Cr coating showed good oxidation resistance. Metallography and SEM results for the 750°C samples were essentially the same as those obtained in the 650°C tests.

- Super 304H exhibited excellent steam oxidation resistance in the 750°C environment but was subject to highly localized surface attack.

- The pre-oxidized Cerablak-coated Grade 92 sample experienced a high weight gain in the 650 °C steam environment. A multi-layered oxide scale (approximately 150 µm thick) was formed consisting of an outer layer of hematite, underlain by a classic duplex oxide of magnetite and an iron-chromium spinel. Some buckling of the hematite layer was observed, however, this layer remained intact. The pre-oxidation step prior to steam exposure appears to have accelerated the formation of the hematite layer since no such layer was observed in previous testing with a similar sample not subjected to pre-oxidation.

- The nickel-base alloys exhibited excellent steam oxidation resistance in the 750°C environment due to the formation of thin, protective chromia films.

Table 1
Summary of Weight Gain Results from Steam Oxidation Tests

Sample	Test Temperature (°C)	Wt. Gain (mg/cm^2)
Grade 92 with Si-Cr layer	750	0.2
Grade 92 with Al-Cr layer	750	0.9
Super 304 H	750	0.3
Grade 92 with Cerablak layer (pre-oxidized in air, 1 hr)	650	8.9
CCA 617	750	0.4
Haynes 230	750	0.2

Table 2
Summary of EDS Analysis Results (Wt. %)

Sample	Fe	Cr	Si	Al	O	Mo	W	Other
Grade 92 Si-Cr 750C								
1 μm depth	60.0	35.2	3.6			1.2	---	
10 μm depth	57.9	34.9	2.6			1.2	3.4	
20 μm depth	72.3	25.5	2.3			---	---	
30 μm depth	70.6	26.4	2.4			0.6	---	
100 μm depth	77.1	20.4	2.2			0.4	---	
150 μm depth	78.7	18.0	1.1			0.4	1.8	
200 μm depth	80.1	16.2	1.0			0.6	2.1	
250 μm depth	83.4	13.9	0.8			0.3	1.6	
300 μm depth	85.1	11.9	0.7			0.3	1.9	
400 μm depth	86.6	10.6	0.4			0.2	2.1	
500 μm depth	86.9	10.3	0.3			0.4	2.1	
525 μm depth	87.7	9.5	0.1			0.5	2.1	
Grade 92 Al-Cr 750C								
1 μm depth	76.4	14.1	---	8.1	---	0.5	1.0	
10 μm depth	77.1	13.9	---	7.6	---	0.3	1.1	
20 μm depth	76.3	14.5	---	7.5	---	---	1.7	
30 μm depth	75.7	14.7	---	7.6	---	0.3	1.6	
50 μm depth	76.2	14.1	---	7.8	---	0.3	1.6	
100 μm depth	77.7	12.5	---	7.6	---	0.5	1.6	
200 μm depth	80.0	10.9	---	6.4	---	0.4	2.3	
300 μm depth	81.6	10.2	---	5.3	---	0.3	2.5	
400 μm depth	82.9	10.0	---	3.8	---	0.4	2.8	
500 μm depth	84.0	9.8	---	2.7	---	0.5	2.9	
600 μm depth	85.5	9.9	---	1.6	---	0.5	2.6	
700 μm depth	86.6	10.0	---	0.7	---	0.4	2.3	
730 μm depth	87.6	9.1	---	0.4	---	0.5	2.5	
Area 1 (surface)	75.4	15.9	---	7.4	---	---	1.4	
Area 2 (white phase)	17.0	72.2	---	0.1	---	2.4	8.3	
Area 3 (interface)	4.8	1.5	4.2	50.1	35.2	2.2	---	1.9 Mn
Area 4 (precipitate)	30.5	7.4	---	53.8	---	---	---	8.3 N

Table 2 (cont.)

Sample	Fe	Cr	Ni	Al	O	Mo	W	Other
Super 304H 750C								
General Area 1 (Fig.9)	16.1	45.9	3.4	---	17.8			11.7 Si, 2.3 Cu, 2.9 Mn
General Area 2 (Fig.9)	71.7	14.4	9.1	---	---			0.7 Si, 3.5 Cu, 0.6 Nb
Area 1 (Fig.10)	41.3	34.3	4.7	---	16.1			3.6 Si
Area 2 (Fig.10)	25.3	52.5	2.2	---	19.1			0.5 Si, 0.5 Nb
Area 3 (Fig.10)	74.2	10.9	12.1	---	---			0.3 Si, 2.6 Cu
Area 4 (Fig.10)	68.3	19.8	8.5	---	---			0.3 Si, 0.1 Nb
Area 5 (Fig.10)	26.6	49.8	4.0	0.2	11.3			6.8 Mn
Grade 92 Cerablak 650°C (pre-oxidized)								
Area 1 (outermost layer)	63.7	---		0.2	31.9	---	---	3.5 Si, 0.4 Na, 0.2 Ca, 0.1 Mg
Area 2 (buckling zone)	63.1	0.1		1.8	31.9	---	---	2.6 Si, 0.2 Na, 0.3 Mn
Area 3 (white rim)	66.5	---		0.2	31.2	---	---	2.1 Si
Area 4 (upper magnetite)	69.0	---		---	30.2	---	---	0.4 Si, 0.4 Mn
Area 5 (lower magnetite)	69.0	0.2		---	30.3	---	---	0.4 Si, 0.1 Na
Area 6 (upper spinel)	50.5	14.6		0.2	30.1	0.6	3.8	0.2 V
Area 7 (lower spinel)	49.2	15.4		0.3	30.2	0.9	3.8	0.3 V
Area 8 (metal/oxide interface)	29.3	27.6		1.3	31.1	---	6.4	1.2 S, 0.7 V, 1.0 Cu, 1.4 Mn
Area 9 (base metal)	86.1	10.1		---	---	0.4	2.6	0.2 V, 0.6 Mn
CCA 617 750°C								
Area 1 (surface oxide)		58.4	1.5	0.1	34.0	---		5.4 Si, 0.1 S, 0.5 Ti
Area 2 (surface penetrations)		9.3	30.3	11.9	31.3	6.1		2.1 Si, 0.7 Ti, 8.1 Co
Area 3 (base metal)		23.0	54.5	1.1	---	8.6		0.2 Si, 0.3 Ti, 11.4 Co
Haynes 230 750°C								
Area 1 (surface oxide)	---	56.8	1.25	0.6	34.0	---	---	5.5 Si, 1.8 Mn
Area 2 (base metal)	1.6	27.3	59.0	---	---	1.3	15.5	0.5 Mn

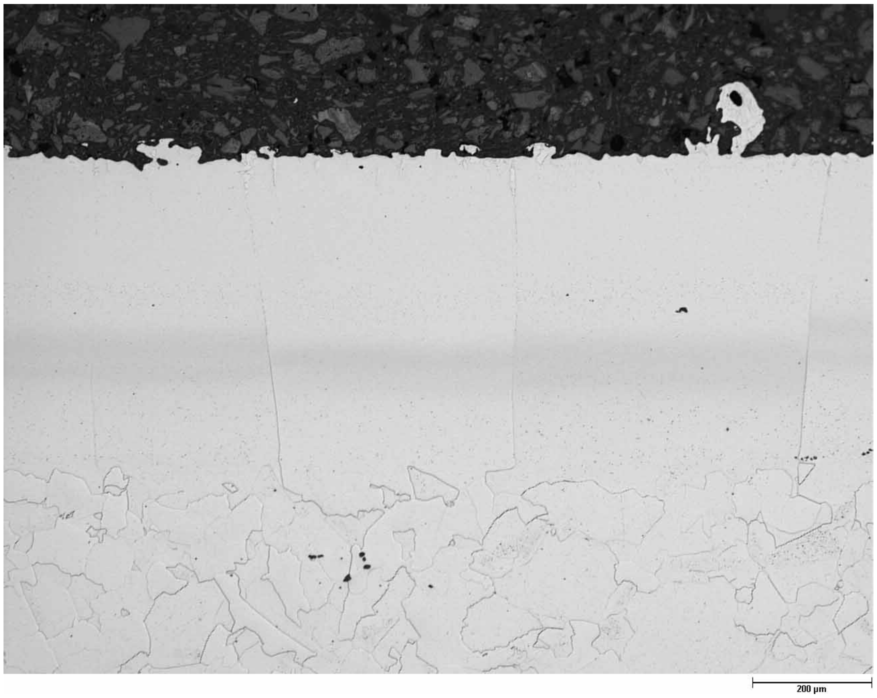


Figure 1: Optical Micrograph of the Grade 92 Si-Cr Sample (750°C)

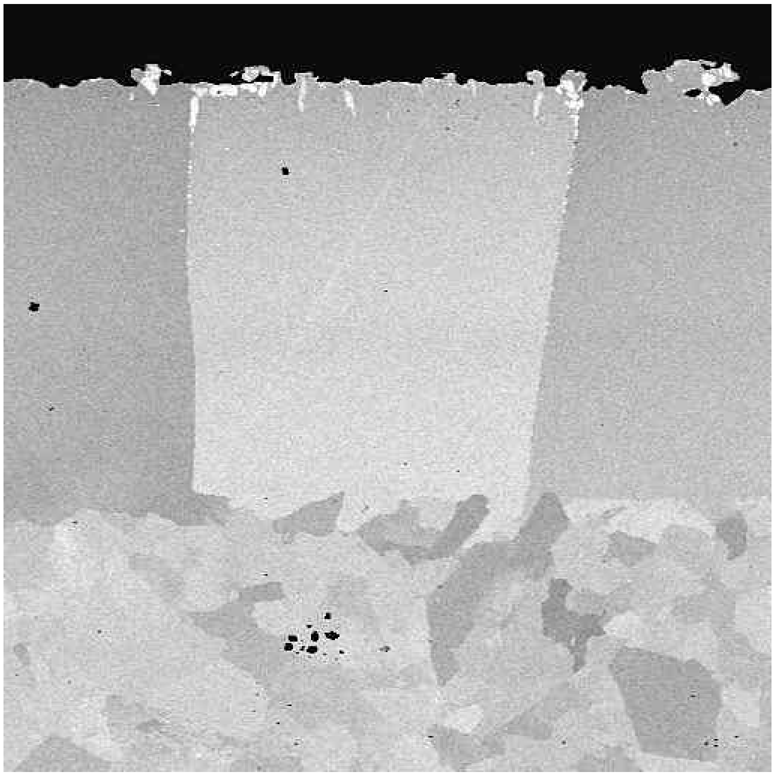


Figure 2: SEM Image of the Grade 92 Si-Cr Surface (750°C)

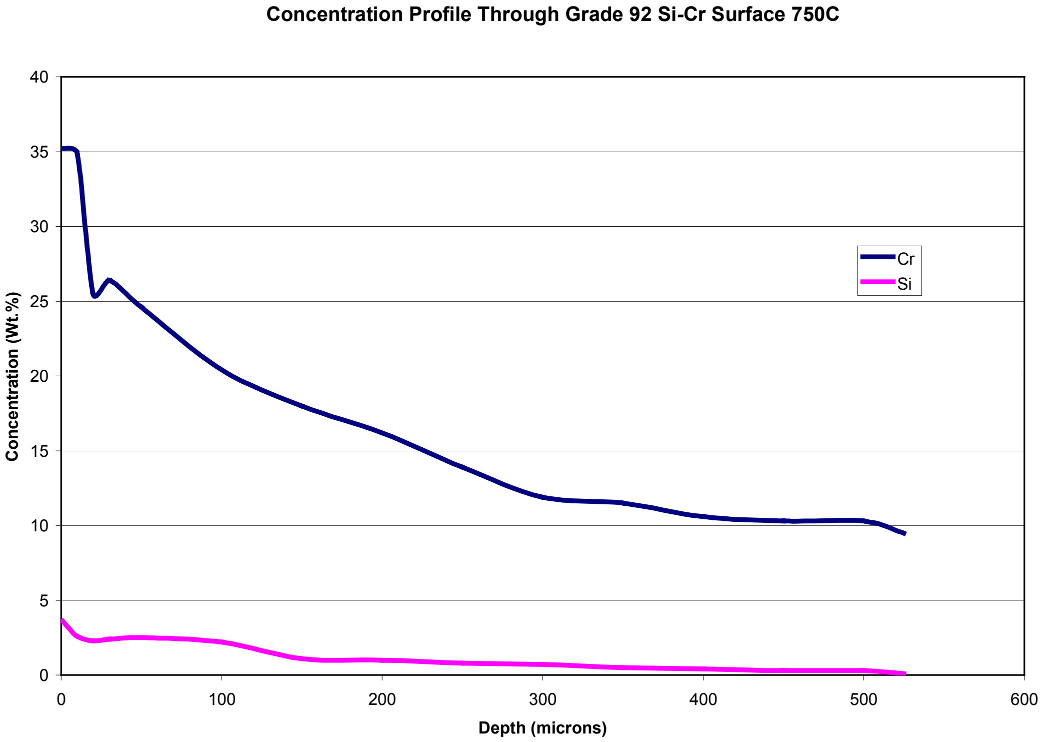


Figure 3: Concentration Profile for Si-Cr Layer on Grade 92 (750°C)

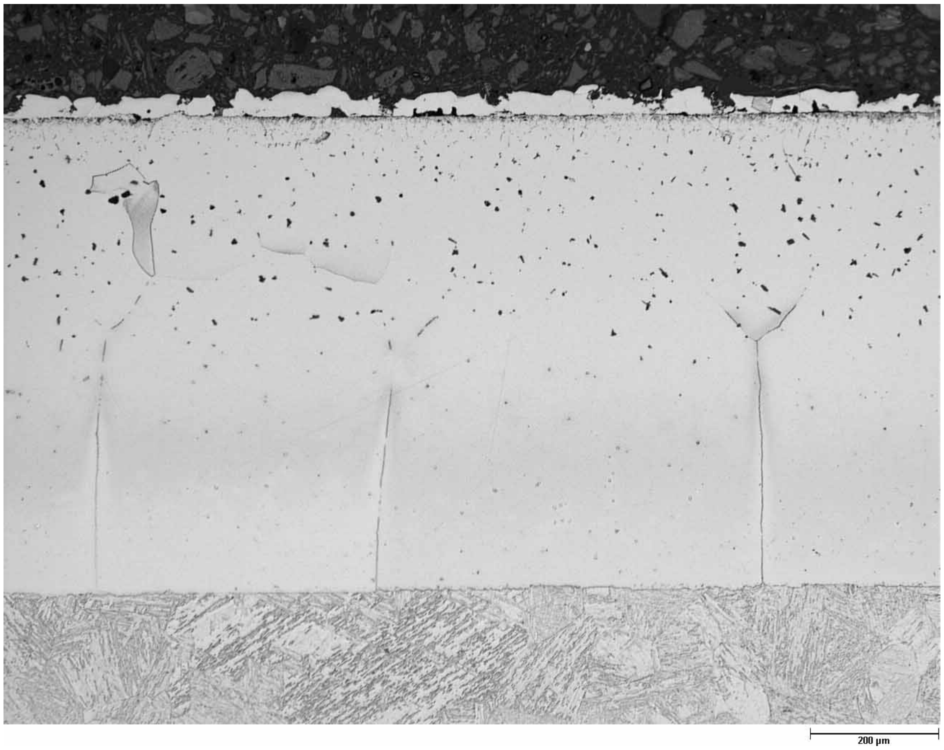


Figure 4: Optical Micrograph of the Grade 92 Al-Cr Sample (750°C)

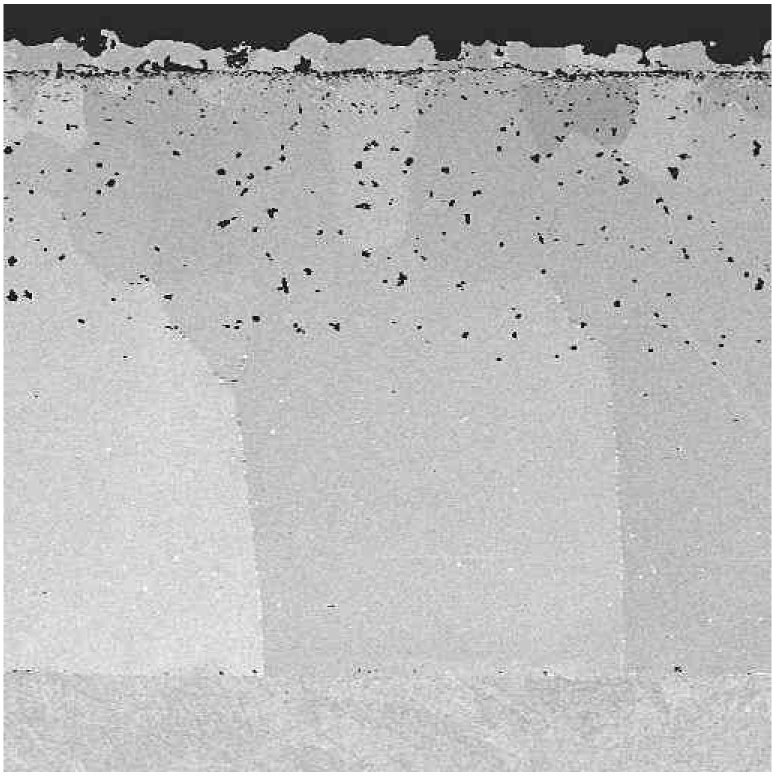


Figure 5: SEM Image of the Grade 92 Al-Cr Surface (750°C)

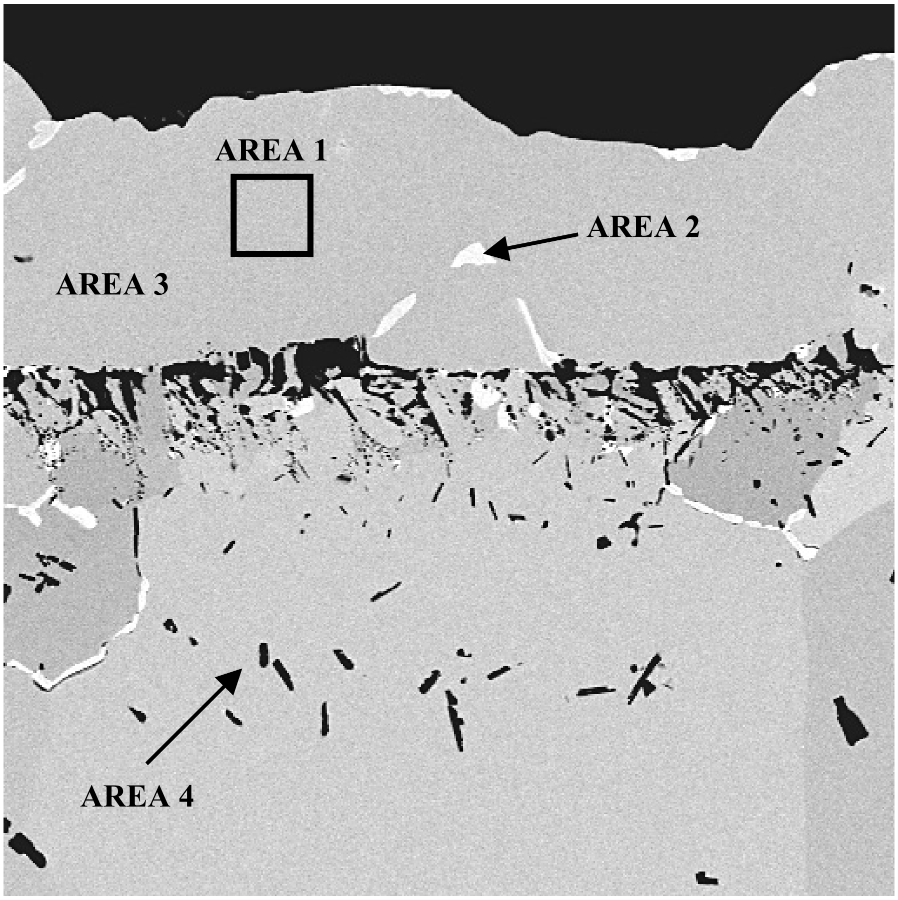


Figure 6: Higher Magnification SEM Image of the Grade 92 Al-Cr Surface (750°C)

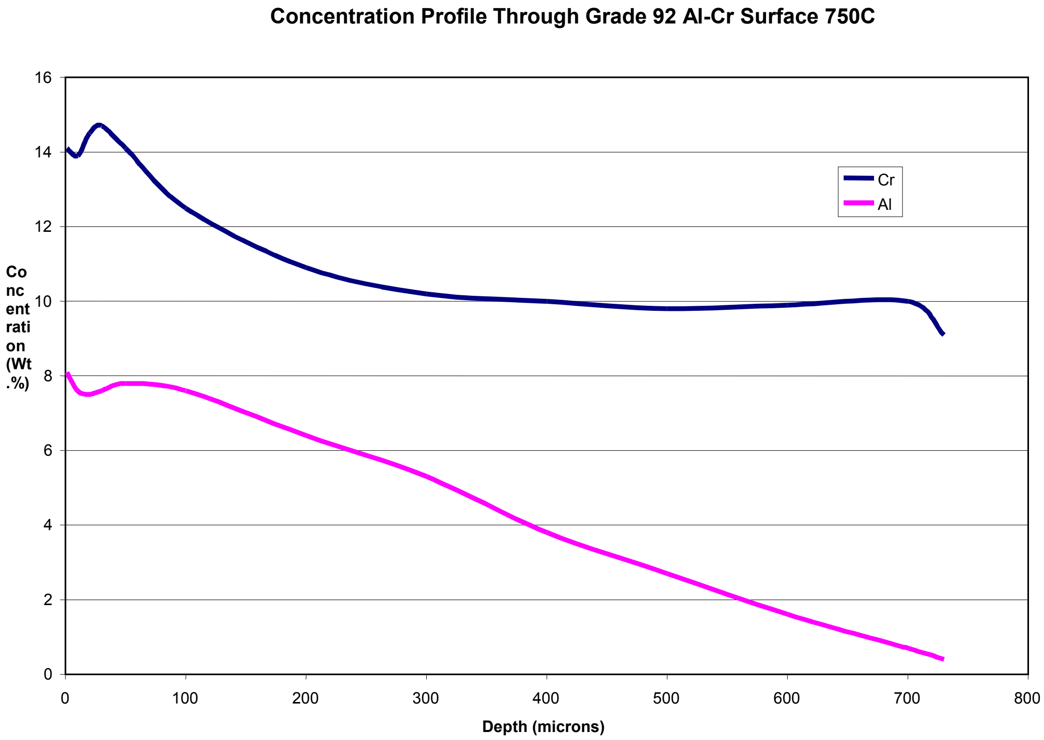


Figure 7: Concentration Profile for Al-Cr Layer on Grade 92 (750°C)

Figure 8: Optical Micrograph of the Super 304H Sample (750°C)

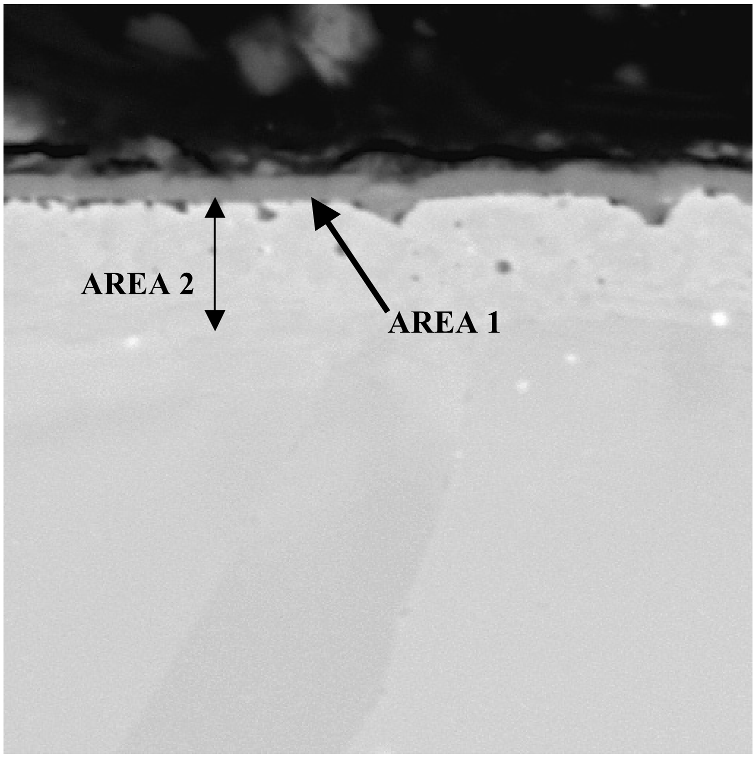


Figure 9: High Magnification SEM Image of the Super 304H Surface (750°C)

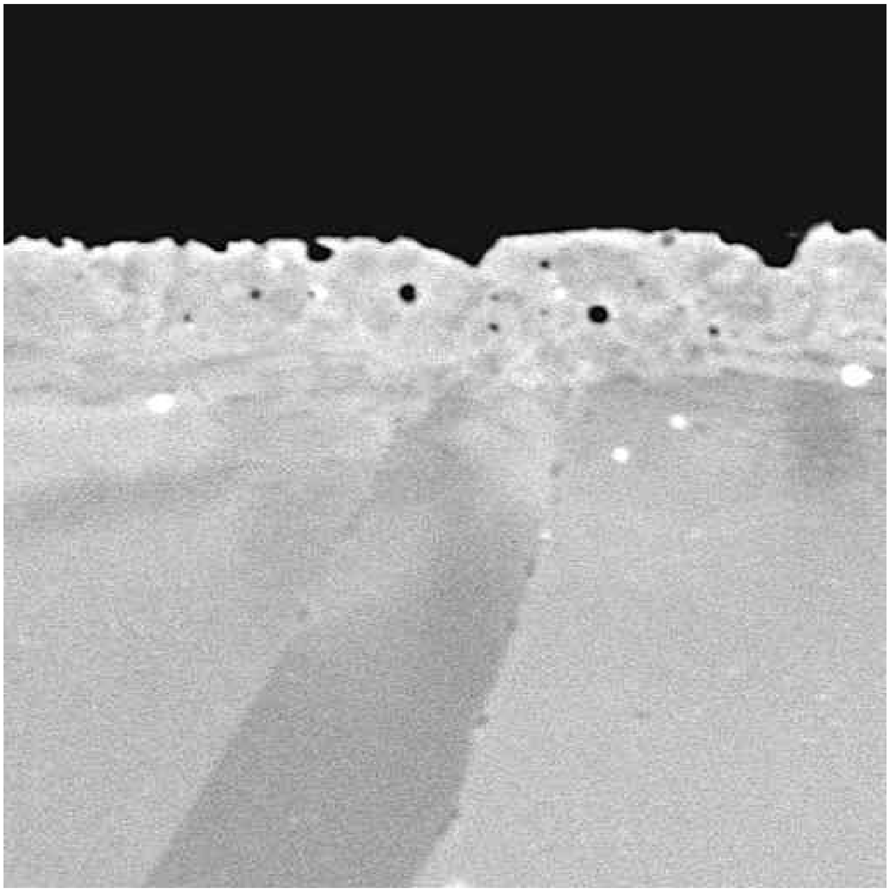


Figure 10: High Contrast SEM Image to Better Illustrate Area 2 Shown in Figure 9 on the Super 304H Surface (750°C).

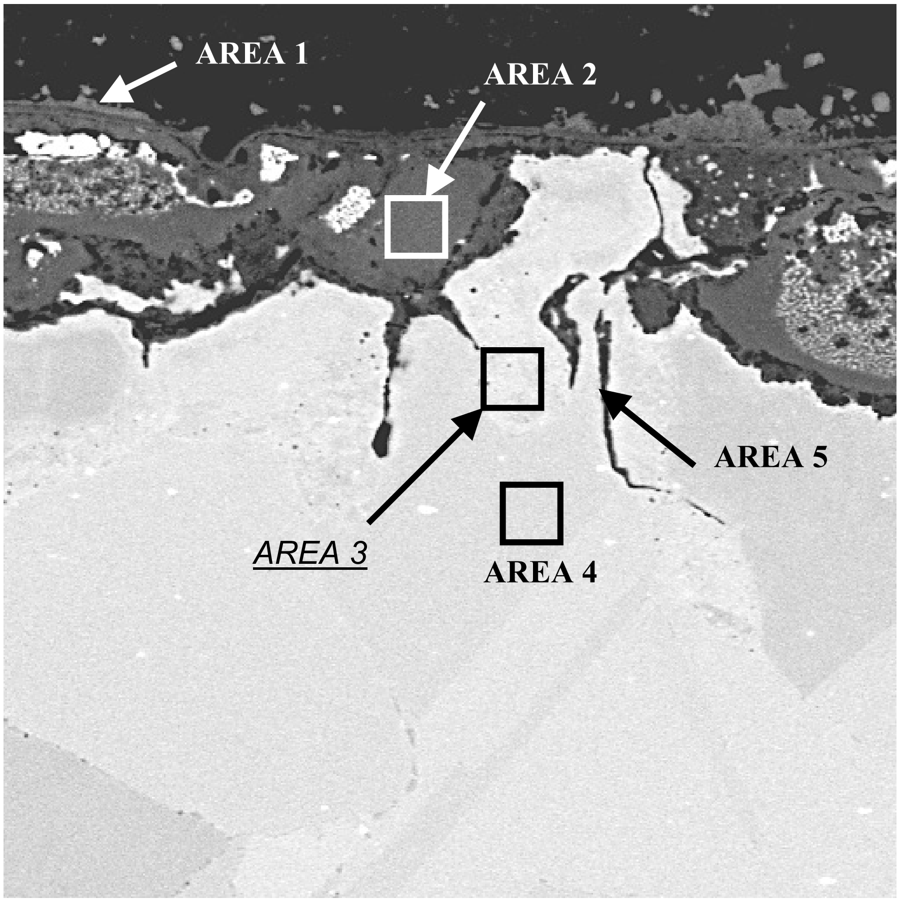


Figure 11: SEM Image from an Area of Localized Attack on the Super 304H Surface (750°C).

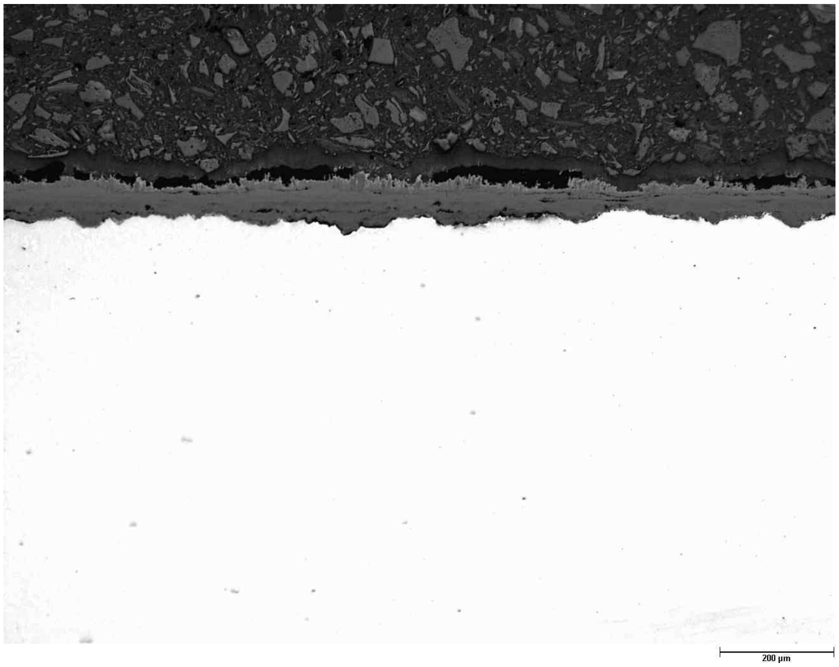


Figure 12: Optical Micrograph of the Grade 92 Cerablak (pre-oxidized) Sample (650°C)

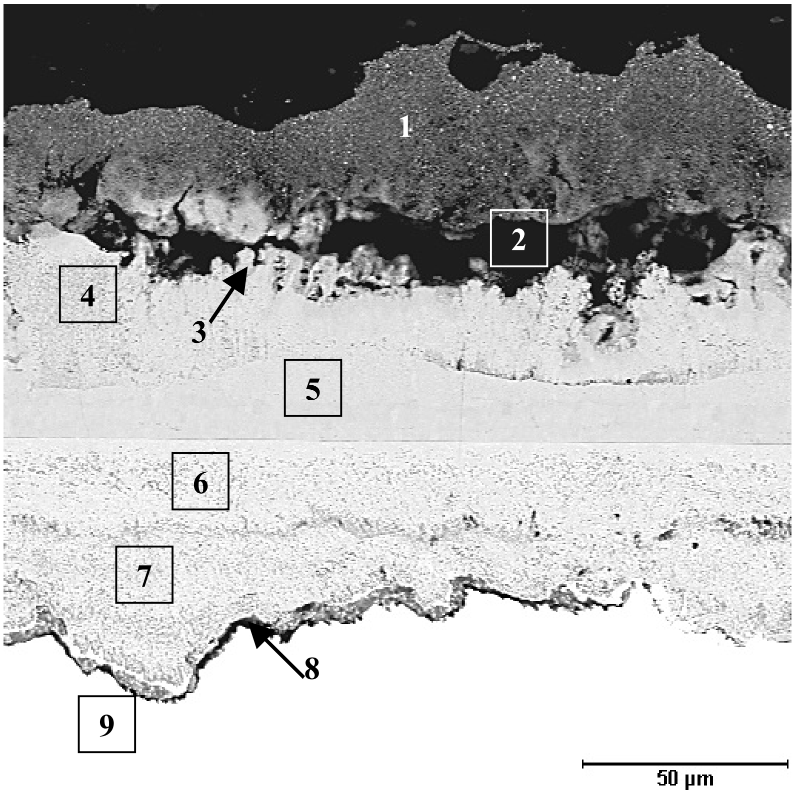


Figure 13: SEM Image of the Grade 92 Cerablak (pre-oxidized) Surface (650°C)

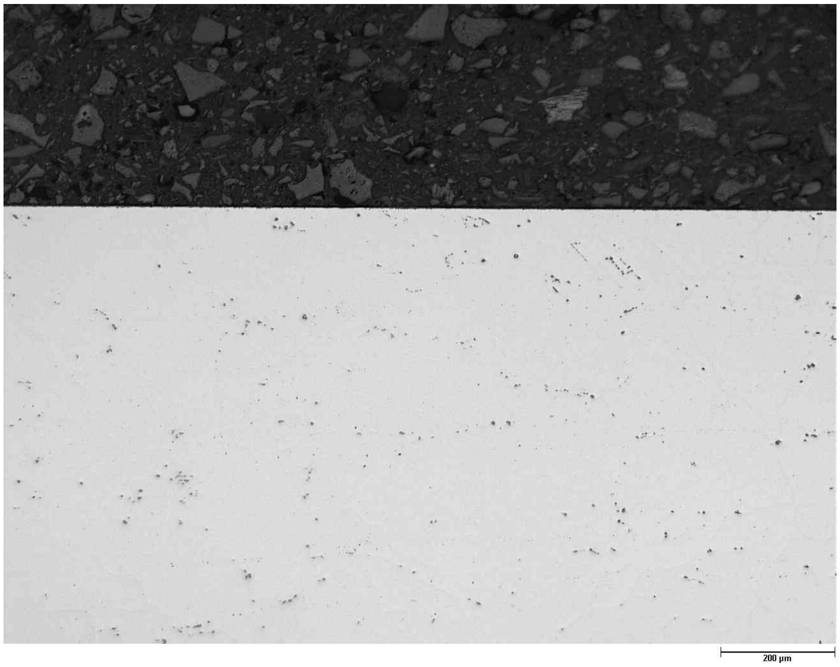


Figure 14: Optical Micrograph of the CCA 617 Sample (750°C)

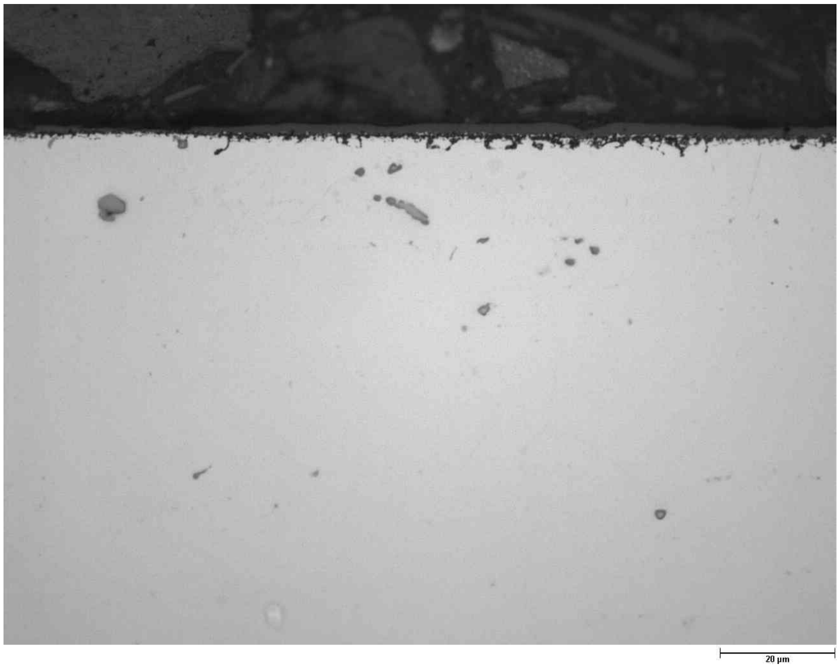


Figure 15: Optical Micrograph Illustrating Thin Oxide on the CCA 617 Surface (750°C)

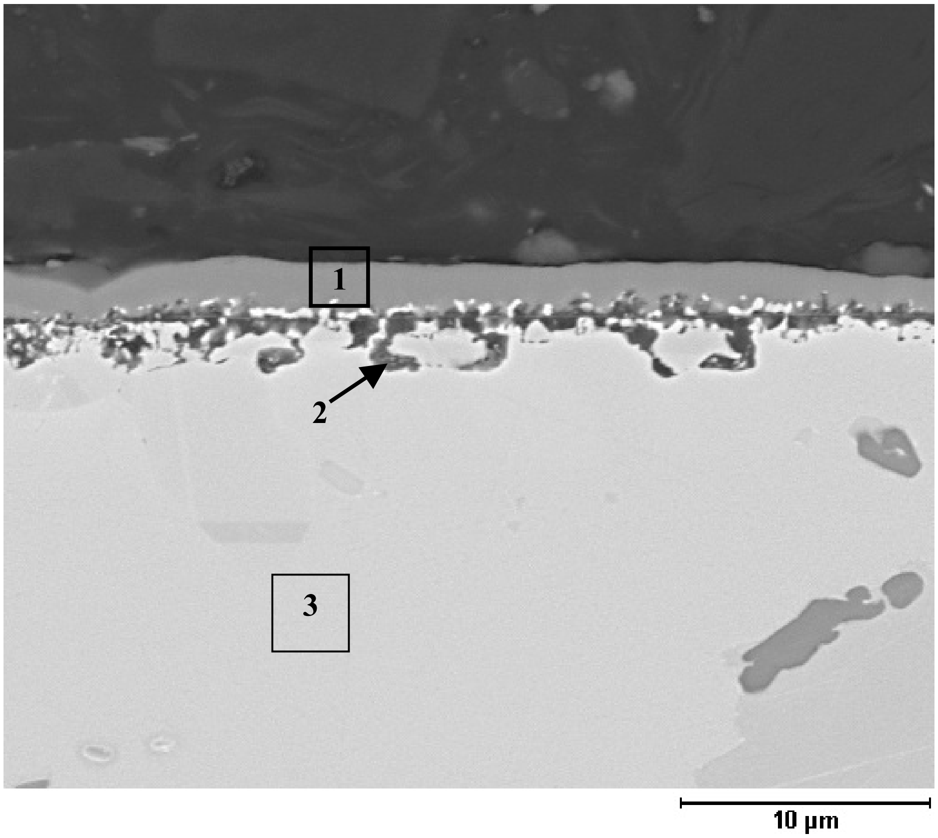


Figure 16: High Magnification SEM Image of the CCA 617 Surface (750°C)

Figure 17: Optical Micrograph of the Haynes 230 Sample (750°C)

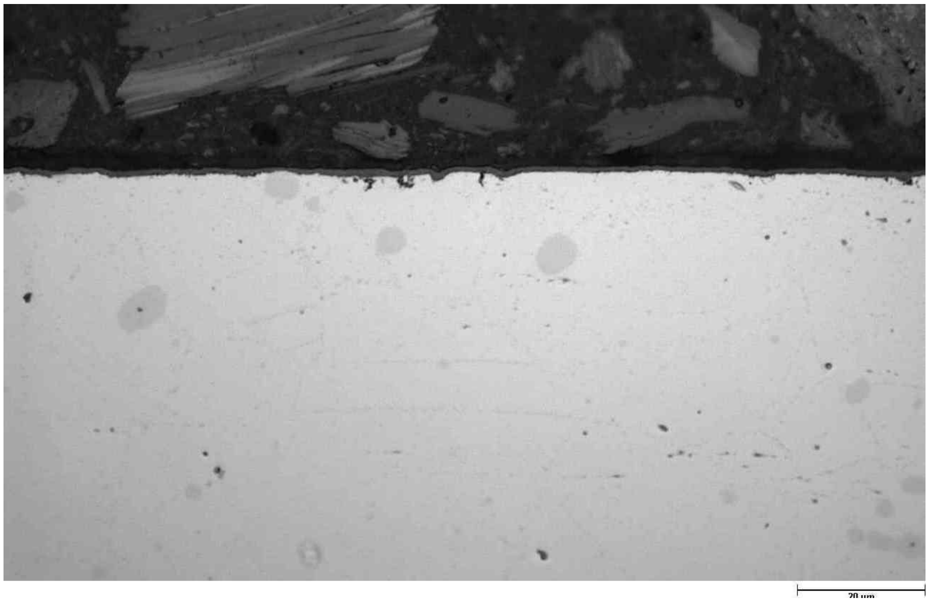


Figure 18: Optical Micrograph Illustrating Thin Oxide on the Haynes 230 Surface (750°C)

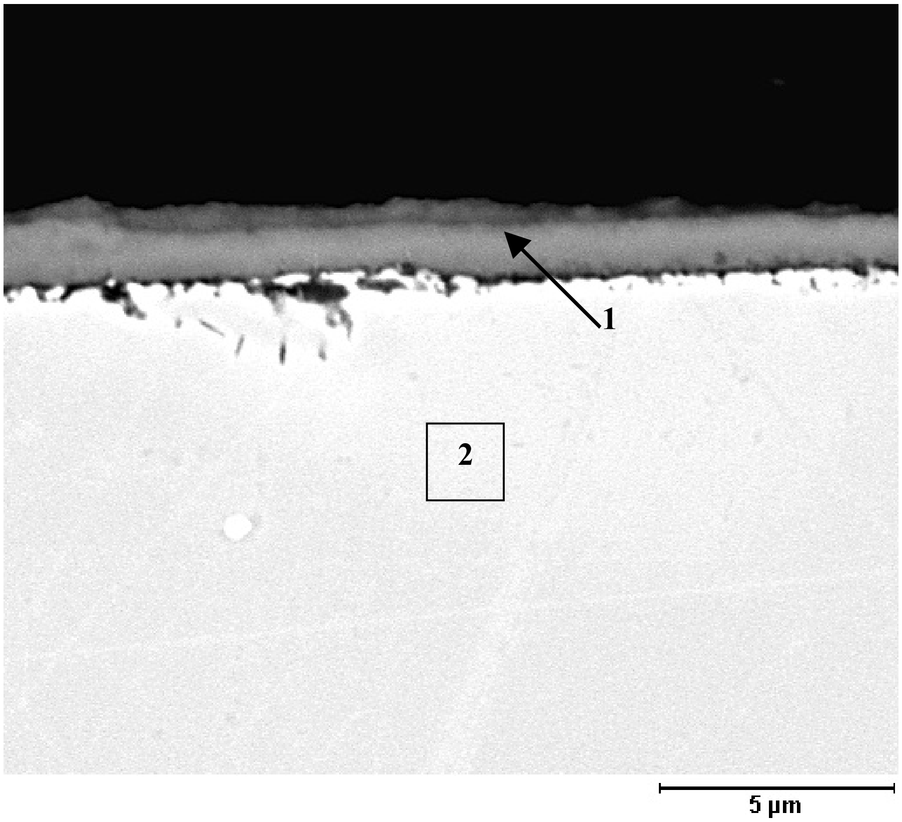


Figure 19: High Magnification SEM Image of the Haynes 230 Surface (750°C)

Appendix II
The Kinetics of Oxidation of Diffusion Coatings in Superheated Steam

Juan Carlos Nava, Stephen Goodstine and Ed Silva

Abstract

The kinetics of oxidation of Cr-rich, Si-Cr-rich and Al-Cr-rich diffusion layers have been studied in the superheated steam within the temperature range 650 and 750 ºC. The diffusion layers were generated in test-pieces of alloy type P-92 using the pack cementation approach. The thermogravimetric analytical technique was used to determine the kinetic in superheated steam over a period of 100 h. The results were benchmarked against the oxidation kinetic of the bare P92 alloy at 650 ºC. The results of these short-term experiments indicated a significant improvement in oxidation resistance where the diffusion layers did not experience any apparent attack. The oxidation kinetics of a test-piece of alloy type S304H was also determined at 750 ºC. The latter type of samples experienced oxidation with the formation of a 1 µm thick Fe-Cr spinel type oxide with discrete patches of break-away oxidation. By comparison, the diffusion layers showed no apparent attack. The diffusion layer chemistry remained stable even at 750 ºC for all coated composition. The characteristics of the diffusion layers will be presented. This work was sponsored by the Department of Energy (DOE), Ohio Coal Development Office (OCDO) and ALSTOM Power Inc.

Introduction

The primary objective of the materials effort in the Ultra-Supercritical boiler program is to provide the most cost effective materials solution(s) to provide adequate component life to maintain a cost-competitive and environmentally acceptable coal-based electric generation. Advanced steam conditions are critical to the efficiency improvements of fossil-fuel power plants. Higher operating temperature results in higher efficiencies, which in turn translate into lower emissions and consequently the requirement for better materials.

1. Apart from adequate strength the following areas are of concern;
2. Adequate oxidation resistance in advanced steam conditions in the temperature range 600 to 900 ºC.
3. Adequate oxidation/sulfidation resistance at the furnace heat transfer surfaces due to microenvironments related to the implementation of in-furnace modified combustion techniques to control NOx emissions.

Adequate oxidation/sulfidation/carburization resistance in the presence of coal ash at reheaters and superheaters.

Most code-approved materials lack the oxidation/corrosion resistance needed to operate facilities in these regimes. Therefore, the commercial deployment of coating processes engineered to target the potential problems outlined above may be the most cost effective approach. The justification of such commercial venture needs, however, to be substantiated with tangible improvements in coatings performance in the whole spectra of possible oxidation/corrosion scenarios. T he performance of the coatings generated during the course of task 7 need to be evaluated under controlled laboratory conditions aimed at simulating the various operating modes of oxidation and corrosion attack.

Feasibility studies are aimed at evaluating the benefits of diffusion type coatings as effective barriers to steam oxidation attack. These various layers vary in composition including straight chromizing, Si-Cr and Al-Cr rich layers. These layers have been generated at the expense of Fe-base alloys, ferritic and austenitic, with minimum distortion of dimension and mechanical properties. Ferritic alloys are subjected to normalizing treatments after the coating process while the coating of austenitic alloys is conducted at their solution annealing temperature. The characteristics of the layers will be discussed after a brief introduction to the phenomenon of steam oxidation.

Steam-side Oxidation

For the same temperature, the oxidation of Fe-base alloys in superheated steam is faster than in air. The oxidation of Fe-base alloys regardless of their ferritic or austenitic, nature follows parabolic kinetic with the formation of a two-layer oxide scale where magnetite, Fe_3O_4, forms as an outer scale while an inner oxide scale of comparable thickness is made, besides Fe-oxide, of oxides of the other alloying elements. The addition of alloying elements such as Cr and Ni seems to slow-down the growth of the outer magnetite layer by perhaps blocking the outward diffusion of the Fe cations. In ferritic alloys the beneficial effect of alloying elements is observed at temperatures in excess of 650 ºC where the contribution of lattice diffusion is comparable to that of grain boundary diffusion resulting in the formation of pseudo-protective spinel oxide phases. For temperatures in excess of 650 ºC the kinetic of oxidation for austenitic alloys is slower than that for ferritic alloys with Cr contents greater than 9 %. The limited data in the oxidation of superalloys in superheated steam suggests that their oxidation can be predicted using existing data from still air exposures at temperatures in excess of 750 ºC.

The use of ferritic alloys is preferred in the lower furnace cavity of coal fired units due to their higher thermal conductivity and relative lower cost. However, although modified low alloy ferritic steels could meet the strength requirements for application at temperatures between 600 and 620 ºC, they lack the adequate resistance to oxidation in steam and in aggressive mixed-oxidant fireside microclimates from high sulfur burning coals. Treated with adequate surface modification, these alloys could meet the stringent requirement of high efficiency coal-fired units.

Various formulations of potential application for the ID and OD of heat transfer surface tubing and piping have being designed. These layers are applied by chemical vapor deposition (CVD) resulting in metallic bonded layers with compositions rich in alloying elements such as Cr, Al and Si that may impart adequate protection in steam containing environments in the temperature range 600 to 900 ºC. The layers can be generated in both ferritic and austenitic Fe-base alloys with minor changes to the dimensions of the original component.

Chromized layers with maximum Cr-contents varying from 20 to 43 wt% Cr can be consistently generated. The thickness of the layers can be modified by controlling the processing time. The thermogravimetric technique can be used to quickly discriminate the effect of Cr-content on steam oxidation susceptibility.

The same technique can be used to discriminate the effect of Si- and of Cr-content in diffuse layers in the same substrates. Layers containing from 2.5 to 8 wt% Si can be generated with the Cr-content varying from 35 to 6 wt%, respectively. There is a synergy between the attainable Si and Cr contents. Similarly, Al-rich layers can be consistently generated with a maximum Al content of 16 wt% that could have a positive impact in the oxidation kinetics in steam.

Samples of T-92 material were coated using the pack cementation technique to generate diffusion layers enriched in Cr, Si-Cr and Al-Cr, respectively. The ALSTOM chromizing formulation was used to generate the chromized layers, while the formulation in patent # 5,972,429 was used to generate the Si-Cr rich diffusion layers. The formulation by M. Zheng and R. Rapp, of public domain was utilized to generate the Al-Cr diffusion layers. The current report summarizes the characteristics of the diffusion layers and presents preliminary data on the oxidation resistance of these diffused layers in superheated steam.

Experimental

Samples of T-92 material of about 2.54 x 1.25 x 0.64 cm (1 x 0.5 x 0.25 inch) were degreased in an ultrasonic bath of ethanol. The weight of the samples was determined using an analytical balance with four decimal places and the measurements were then recorded. A pack of the required composition was mixed and then milled for 10 min. The samples were embedded in the pack using 3.5 g of pack powder per square centimeter of surface area to coat. The packing powder and the samples were contained in alumina castable cylinders closed with a lid with three minute holes for venting purposes. The coating temperature was 1140 ºC with a holding time of 16 h. The samples were furnace cooled and removed from the pack. The samples were then washed in soapy water and rinsed in an ultrasonic bath of ethanol. Their post coating weight was measured and then recorded.

The characteristics of the coating were determined using optical microscopy in a transverse cross-section of control samples. The scanning electron microscope with an EDS attachment was used to determine the composition profiles.

The kinetics of steam oxidation was determined using the thermogravimetric technique. The microbalance had a wide range of weight change scales up to 100 mg. Steam was generated by pumping deaereated water through a heater attached to a stabilized silica reactor chamber with the samples suspended in a constant heat zone of approximately 5 cm. Tests were conducted isothermally over a period of 160 h.

Results

Diffusion Coatings

1. Chromized samples

Figure 1.a is a Back-scattered electron image of the chromized layer in the archive sample. The surface of the samples does not show the formation of a chromium carbide surface layer and the grain boundaries of the columnar grains are apparently free of Cr-carbide precipitates. The subsurface porosity is the result of the Kirkendal effect and it is limited to within 40 µm from the surface. The coating thickness is in average 450 µm with a maximum average Cr-concentration of 32 wt%, Figure 1. Decarburization of the substrate was not apparent.

2. Si-Cr diffusion layers

The characteristics of the Si-Cr diffusion layer are depicted in Figure 2.a. The Back-scattered electron image revealed clean grain boundaries and columnar-type grains. The EDS analyses confirmed a the absence of a Cr-carbide surface layer and the maximum average Si and Cr contents are 2.3 and 30 wt%, respectively. The average coating thickness is about 500 µm. Figure 2 shows the average Si and Cr concentration profiles.

3. Al-Cr diffusion layers

Figure 3.a depicts the diffusion layer. There is an outward growing layer about 30 µm thick with an average Al and Cr content of 8 and 16 wt%, respectively. This outward growing layer is not continuous since it tends to fell off during handling due to the weak bonding to the inner growing layer. Fine alumina particles are usually found at the interface between both layers and this causes the outer layer to spall off. The inner growing layer shows an array of precipitates made of Al-nitride.

Figure 3 shows the average concentration profiles for Al and Cr across the layer. The coating thickness is about 700 m µ. As a reminder, this layer was generated using the qualified formulation by Rapp but extending the processing time to 16 h. Processing periods shorter than 16 h are unrealistic from the point of view of the infrastructure required to heat up large loads of tubing. An increase processing time has resulted in a lower nominal concentration for Al across the layer. Our target was 10 wt% or higher maintaining at least the same Cr-content of the base alloy. Processing times of 6 hours delivered layers with Al-contents between 10 and 14 wt%. There was significant scattered in the concentration profiles by as much as ± 2 wt%. The longer process time apparently reduces the scattered generating layers that are more consistent in thickness and composition.

Kinetics of Oxidation

Figure 4 shows the weight change as a function of the square root of the exposure time for a sample of P-92 exposed to superheated steam at 650 C. The trend suggests parabolic kinetics for the oxygen uptake. Figure 5 depicts the morphology of attack. The outer growing layer was a Fe-oxide while the inner growing layer was an oxide containing Fe, Cr and W in a proportion similar to that present in the base metal. The outer growing oxide is suspected to be magnetite. The EDS unit is not able to discern between Fe_2O_3 and Fe_3O_4 but the spalled flakes were magnetic suggesting the presence of magnetite. The weight changes for a sample of S304H and for the coated P-92 samples are also presented in Figure 4 indicating a significant improvement in the oxidation resistance as compared to P-92. Destructive evaluation of the S304H revealed localized attack at discrete locations resembling the appearance of breakaway corrosion.

The coated samples were exposed at 700 and 750 C to evaluate the oxidation resistance of the diffusion layers. Bare P-92 has not enough strength for structural applications above 620 C. The diffusion layers showed no apparent sign of attack and no indication of breakaway corrosion. Figure 6 shows the trend for the weight change as a function of the square root of time for the chromized, Si-Cr and Al-Cr diffusion layers. Although the destructive analysis did not reveal any form of degradation there was an apparent oxygen uptake. The largest uptake was registered by the Al-Cr coating. The absorption of oxygen is typical of Fe-aluminide type of material at these temperatures with no apparent formation of oxide products. The lack of apparent attack at 750 C confirms the outstanding protection provided by the diffusion layers.

Figure 7 depicts the trend for the oxygen uptake for both the S304H specimen and the chromized P-92 sample at 750 C. The same scattered is apparent from both set of data points with weight gains less than 0.3 mg/cm2. The destructive analyses of the S304H specimen revealed an oxide less than 1 μm in thickness, Figure 8. The EDS of analyses was not accurate since the diameter of electron beam exceeded the thickness of the layer indicating a contribution from the underlying metal chemistry.

Conclusion

- Diffusion layers rich in Cr, Si-Cr and Al-Cr generated in a P-92 substrate provides a significant reduction in oxidation susceptible when exposed to superheated steam in the temperature range 650 to 750 C.

- The behavior of the diffusion layers is comparable to that of S304H but with no apparent general or localized attack.

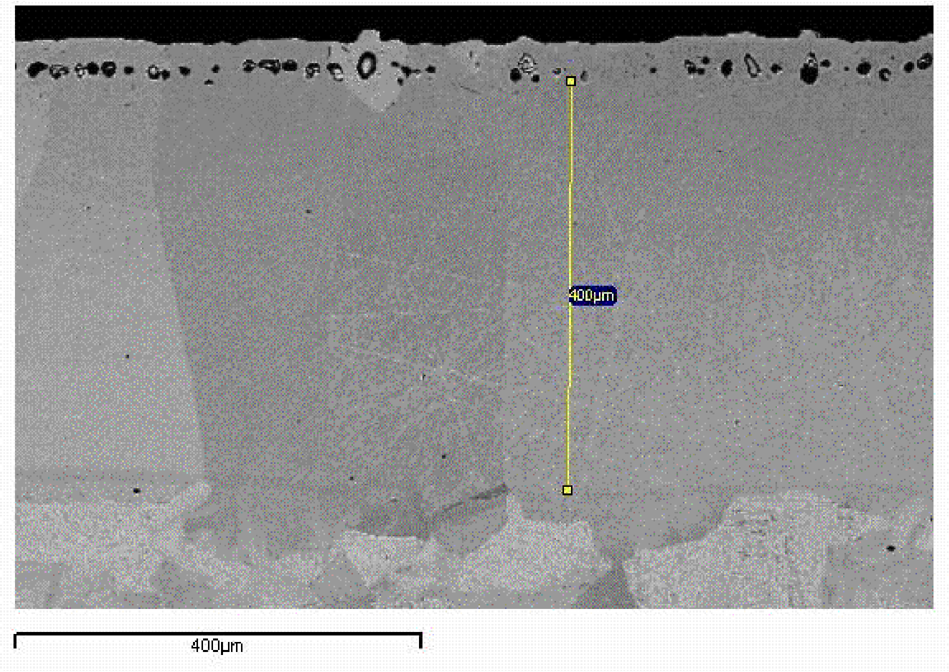


Figure 1a: Backscattered image from the chromized layer generated on a testpiece of P-92.

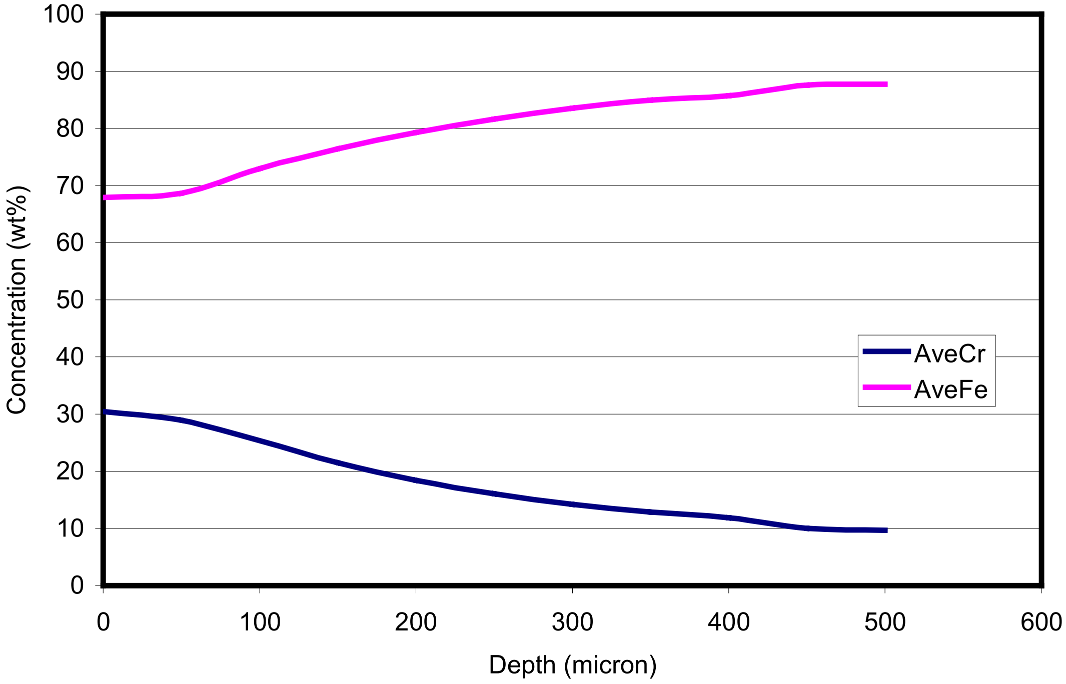


Figure 1b: Average Cr and Fe concentration profiles in chromized layers generated in alloy T-92 to be used in TGA experiments

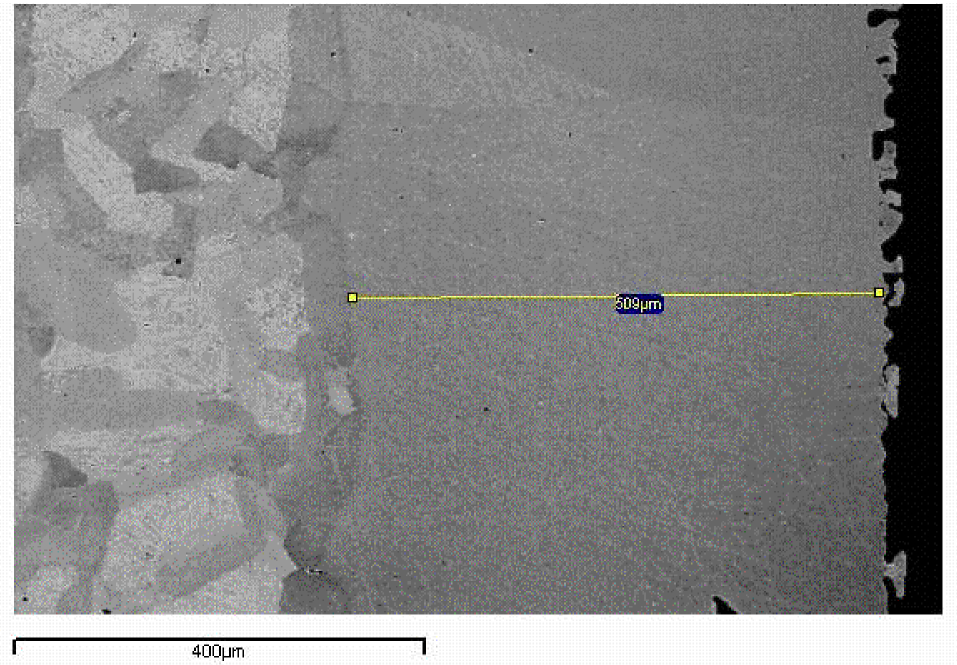


Figure 2a: Backscattered image from the Si-Cr rich diffusion coating generated on a test-piece of P-92 alloy.

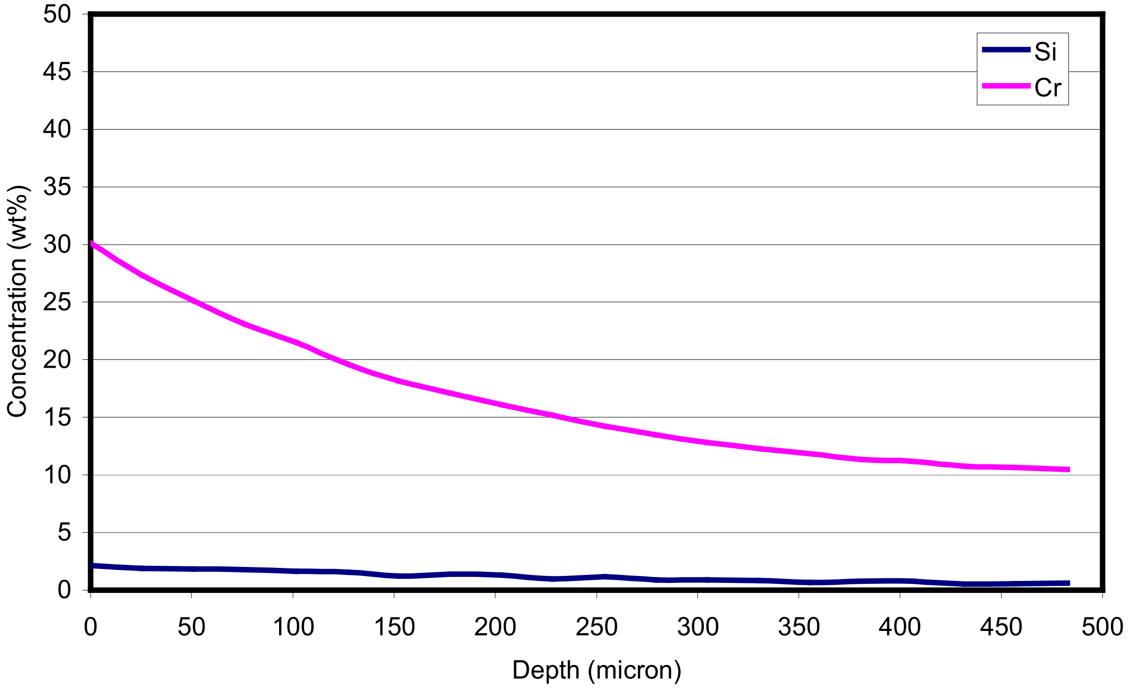


Figure 2b: Si and Cr concentration profiles in diffusion coating generated in T-92 using Si-Cr pack and cementation approach. Sample to be used in TGA studies.

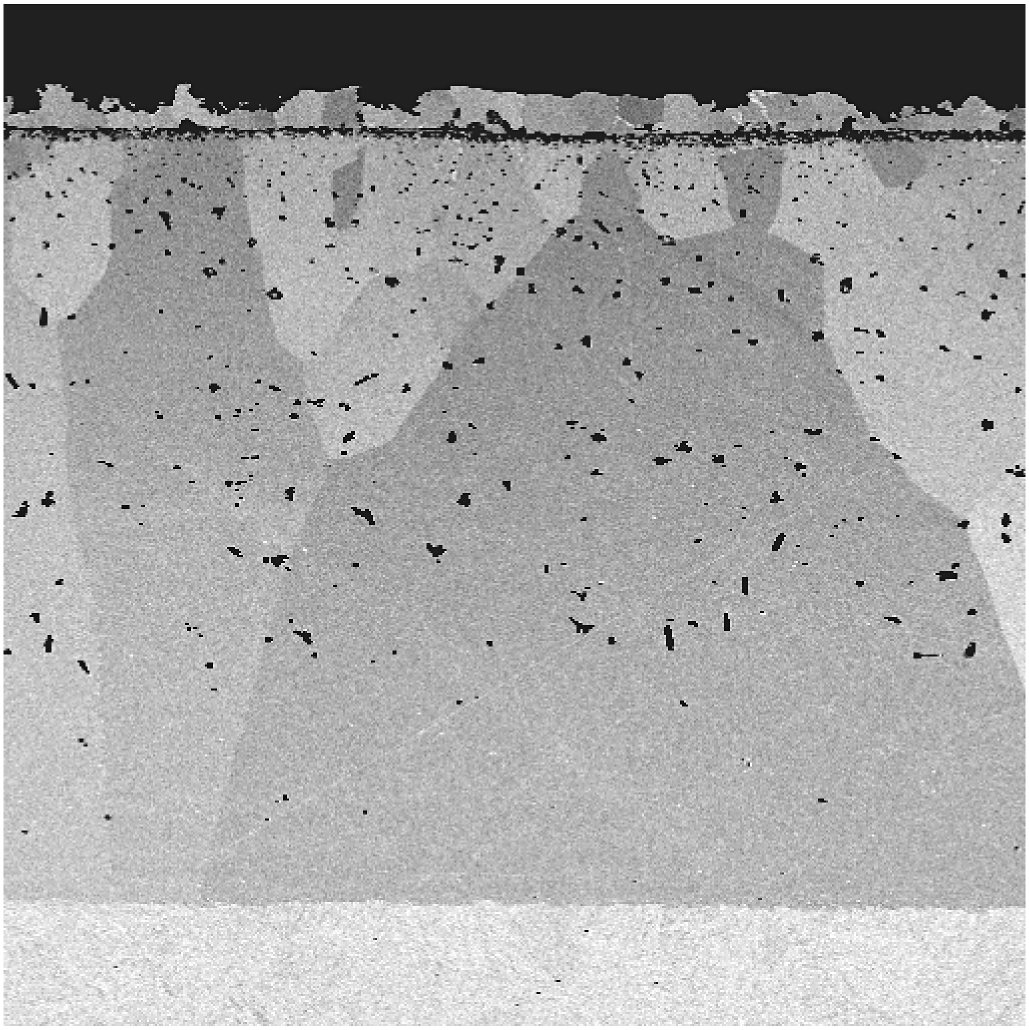


Figure 3a: Backscattered image from the Al-Cr rich diffusion layer generated in a test-piece of P-92.

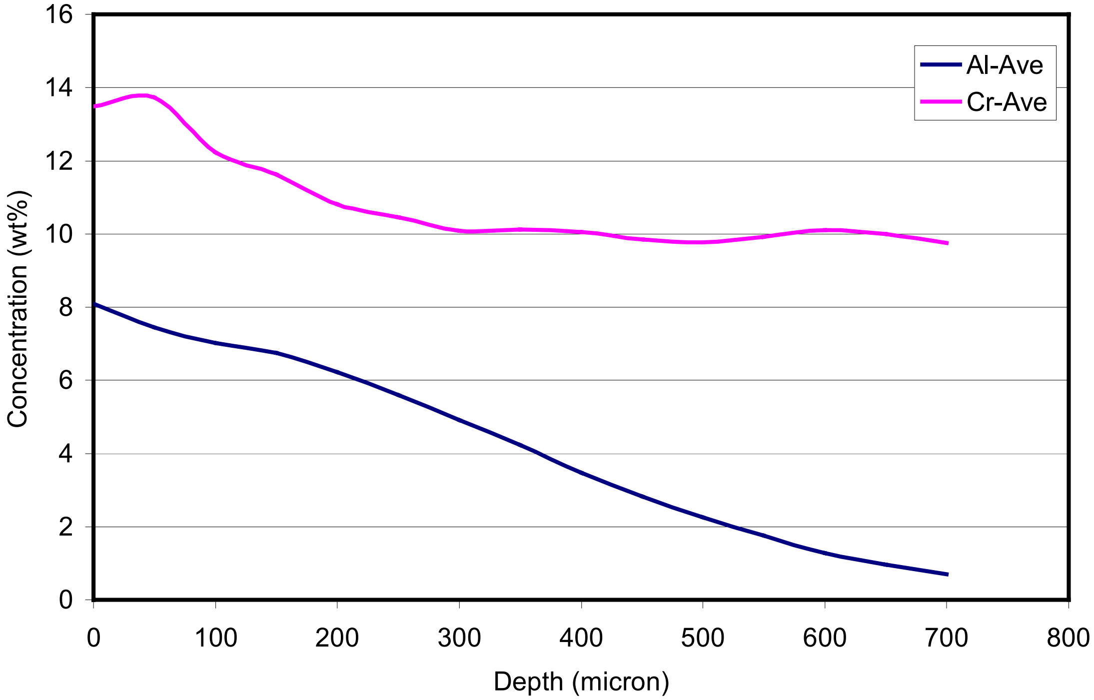


Figure 3b: Average Al and Cr concentration profiles through diffusion layer generated in T-92 material.

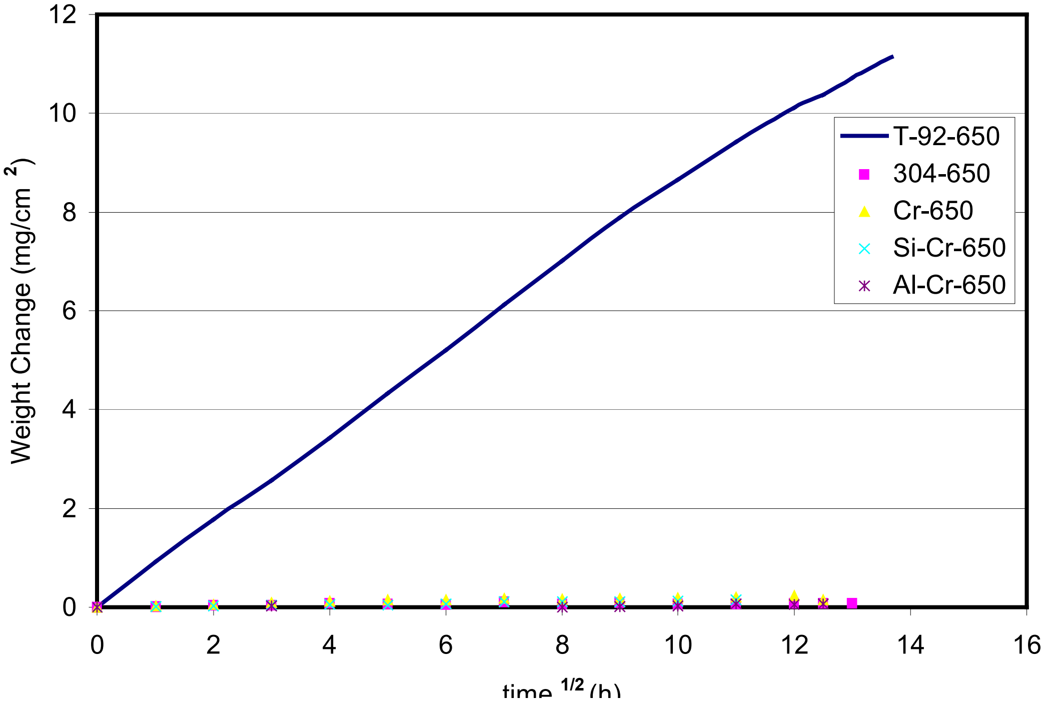


Figure 4: Oxidation kinetics of bare P-92 compared with that of S3O4H and coated P-92 samples. 100 h of oxidation in superheated steam at 650°C

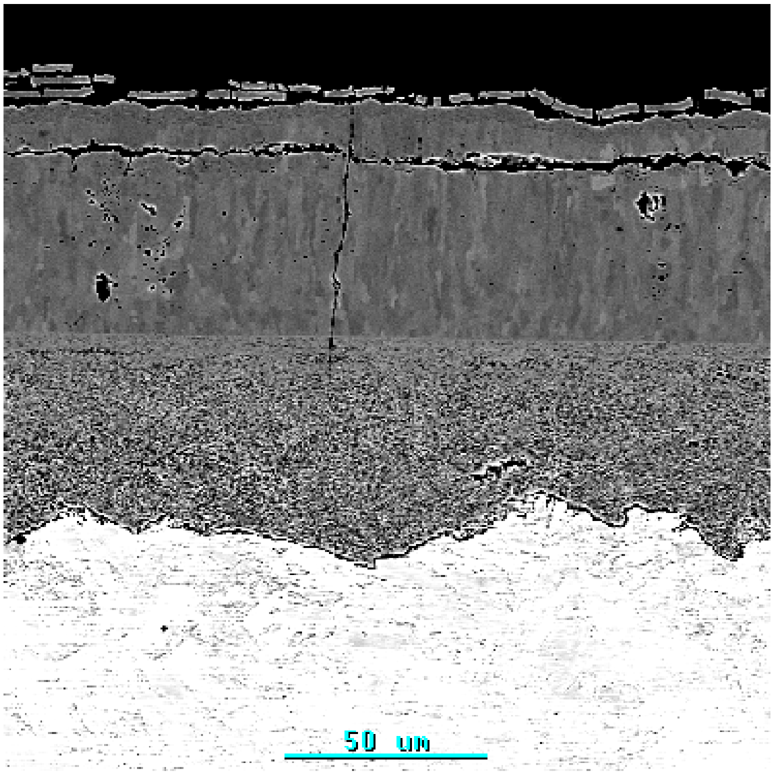


Figure 5: Backscattered image from the oxide layer formed on a test-piece of bare P-92 alloy upon exposure to superheated steam at 650°C.

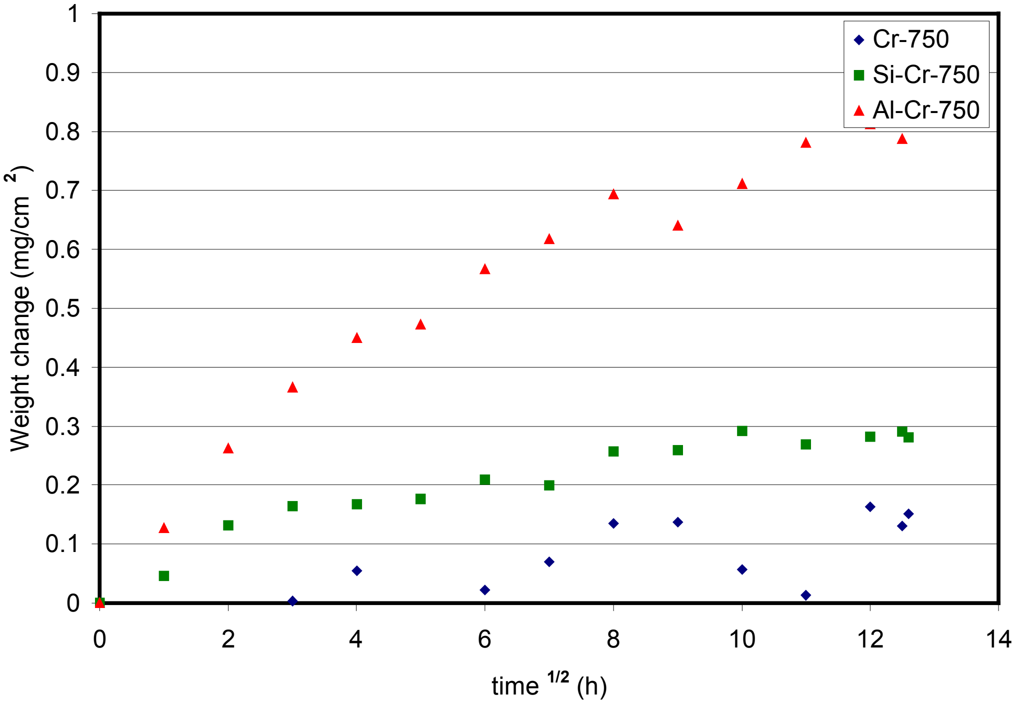


Figure 6: Oxidation kinetics for the diffusion layers in superheated steam at 750°C

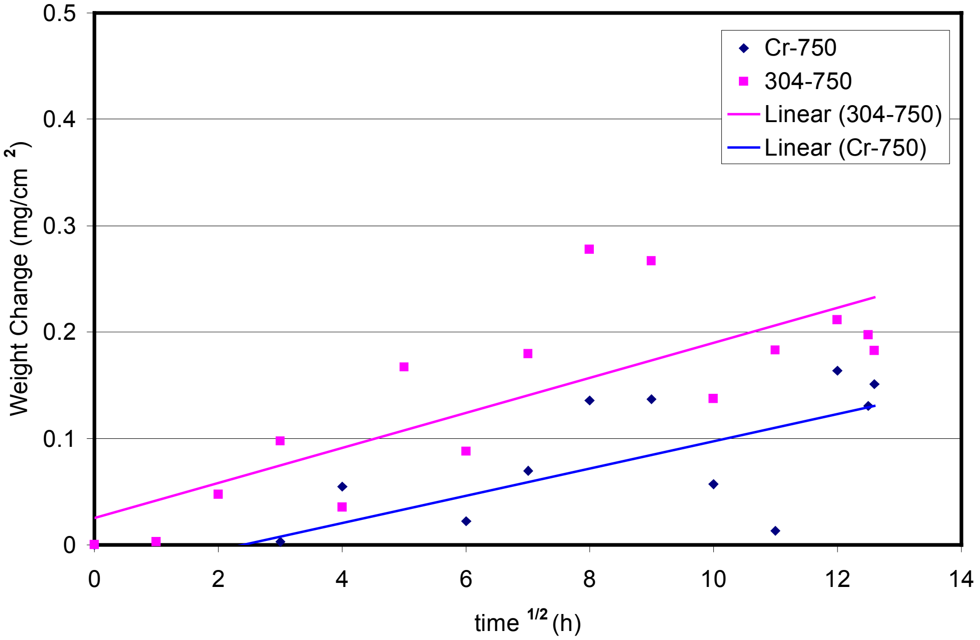


Figure 7: Comparison of the oxidation kinetics in superheated steam at 750°C for chromized P-92 and bare S304H

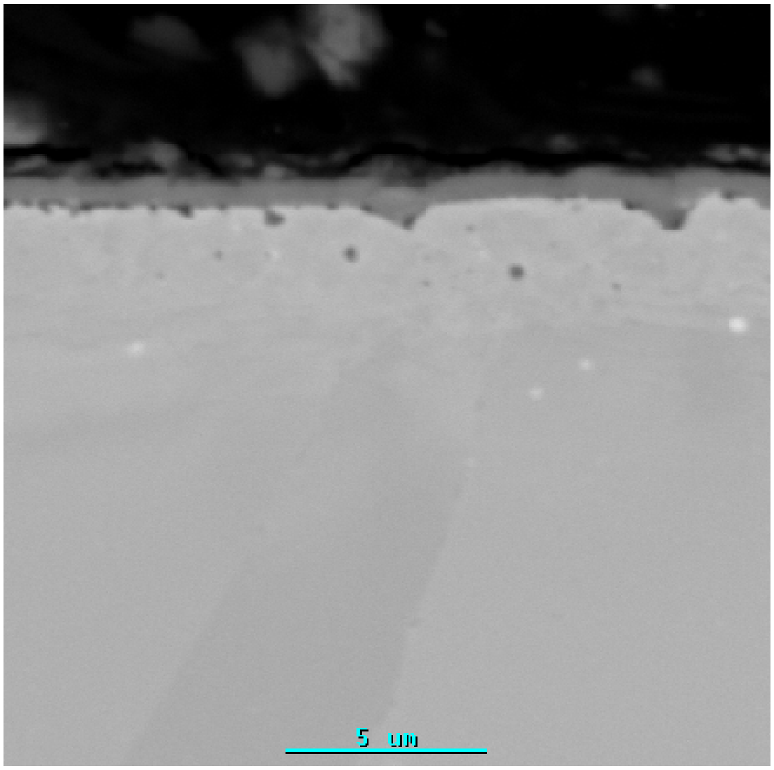


Figure 8: Backscattered image from the oxide layer formed on a test-piece of S304 H alloy upon exposure to superheated steam at 750 °C.

Task 8
Design Methods and Data
(ALSTOM)

The major objectives for Task 8 are:

- Review the methods used by Section I of the ASME Boiler and Pressure Vessel Code to utilize materials properties and behavior models in the design of ultra-supercritical boilers.
- Develop and document methodologies whereby the results of the other tasks within this program may be most effectively applied within the ASME Section I design environment.
- Pursue the incorporation of such methodologies into Section I.

These objectives will be accomplished through execution of seven sub-tasks. Where activity on these sub-tasks occurred during the reporting period, it is described below.

Task 8A: Task Management (ALSTOM)

Objective

The primary objective of this subtask is the overall management of the task, coordinating meetings and preparing progress reports.

Progress for the Quarter

- Continued efforts to resolve workscope issues and technical contributions from participants. Some progress has been made with Babcock and Wilcox and Riley providing a response to the request for comments on the work packages suggested by ALSTOM. No firm commitments have been established. Foster Wheeler has provided no input.
- The Gantt chart for Task 8, showing the overall plan and progress to date is included in Appendix A.

Concerns

Work scope issues need to be resolved next quarter if overall progress is to be unaffected. Contribution of Foster Wheeler needs to be determined and their work scope reassigned if necessary.

Plans for the Next Quarter

A meeting of the Task 8 participants will be held early in the Quarter in an effort to resolve work scope issues and distribution of funding between participants.

Task 8B: Material Data Collation and Processing (Unassigned)

Objectives

The creation of documentation to ensure that quality test data is transferred between tasks and that this data remains traceable. A second objective is the analysis of such data with the objective of improving the statistical correlations.

Deliverables

Item	Responsible	Status
Material data transfer sheets	ALSTOM	Transfer sheets provided for creep and tensile tests.
Electronic data repository	ORNL	No progress to report.
Recommendations for statistical analysis of data		
Data compendia and fits for key materials		
Code case packages and submissions to code committees		

Progress for the Quarter

No progress to report this quarter.

Concerns

No lead investigator yet identified. No progress reported by ORNL on the implementation of an electronic data repository (web or ftp site) for material test data.

Plans for the Next Quarter

Assign sub task leader and ensure that ORNL works to make test data available in electronic format.

Task 8C: Design Rules (Unassigned)

Objective

Develop and present to ASME, alternative design rules incorporating the outputs of the other tasks and subtasks.

Deliverables

Item	Responsible	Status
Report on overall accomplishments for subtask		
Design rules (code case) for unwelded parts		
Design rules (code case) for parts with similar metal welds.		
Design rules (code case) for parts with dissimilar metal welds.		

Progress for the Quarter

There will be no progress on this sub-task until the outputs of other Tasks and subtasks are available.

Concerns

None.

Plans for the Next Quarter

None.

Task 8D: Reference Stress Methods (ALSTOM)

Objective

Develop and issue a description of reference stress methodology and its application to ASME geometries.

Deliverables

Item	Responsible	Status
Topical report on reference stress methods including compendium of solutions.	ALSTOM	Complete (Aug 2003)
Example ASME problem showing use of reference stress and comparison with "full" analysis.	ALSTOM	Complete (Sept 2003)

Progress for the Quarter

The topical report on the reference stress method was completed and distributed. The contents of the report included an introduction to limit analysis and reference stress methods, advice on the calculation of limit load using finite element analysis, advice on the use of reference stress for creep life predictions and a compendium of reference stress solutions.

A set of PowerPoint slides to demonstrate and compare various life assessment methodologies for a nozzle was completed and distributed. The nozzle geometry met the present requirements of ASME Section I and therefore provides a useful benchmark to evaluate analysis methods and variability in life estimates. Some of the PowerPoint slides are included here as Appendix B to illustrate the nozzle geometry, modeling work and life estimates.

The deliverables for this task have been finalized and, therefore, this task is complete.

Concerns

None.

Plans for the Next Quarter

None; task complete.

Task 8E: Continuum Damage Mechanics (Unassigned)

Objectives

The objective of this subtask is to analyze uniaxial and multiaxial creep test data from Task 2 for several (three) materials to:

- establish the continuum damage mechanics (CDM) parameters,
- evaluate multi-axial strength theories and failure criteria,
- create deformation and fracture maps.
- evaluate and compare CDM, reference stress and Omega models of typical ASME geometries.

Deliverables

Item	Responsible	Status
Report to summarize data fitting of CDM parameters for physically based on Omega creep models, including multiaxial parameters.		
Report containing deformation and fracture mechanism maps for each material		
User material subroutine for use with finite element code (e.g. ABAQUS)		
Report to summarize the analysis and validation tests and component simulations, including comparisons between approaches (CDM, Omega, reference stress, etc.)		

Progress for the Quarter

None – technical activities are scheduled to start in Jan 2004.

Concerns

No lead investigator yet assigned. Availability of material data in electronic format.

Plans for the Next Quarter

Resolve division of work scope and assign subtask leader.

Task 8F: Weld Analysis and Assessment (ALSTOM)

Objectives

Create simplified analysis models of welds and heat affected zones (HAZ) utilizing material properties obtained from the open literature and from Task 2 to permit accurate creep life assessment of weldments.

Deliverables

Item	Responsible	Status
Topical review of weld analysis and assessment in creep range.	ALSTOM	In progress.
Collation of material data for weld metal and HAZ.		
Creep models for weld metal and HAZ regions.		
Report documenting the simulation of welded specimens and common Code geometries.		
Report documenting the development and use of approximate weld assessment methods.		

Progress for the Quarter

Initiated topical review of weld analysis methods. A literature search has been performed and a number of relevant papers identified. Relevant sections of other design codes, such as R5, are also being reviewed. Riley Power has offered to contribute to the activities of this task.

Concerns

None.

Plans for the Next Quarter

Continue literature review and being collation of data for weld metal and HAZ regions.

Task 8G: Basic Design Rules for Unpenetrated Cylinders (ALSTOM)

Objectives

Review the various equations used by the ASME Code, Section I for Power Boilers to define the minimum thickness of unpenetrated cylinders under internal pressure and develop a single methodology applicable to ultrasupercritical boilers.

Deliverables

Item	Responsible	Status
Report summarizing existing approaches and comparing and contrasting their predictions	ALSTOM	Complete (Aug 2003)
Report recommending a single equation with supporting theoretical data.	ALSTOM	Complete (Sept 2003)
Code case submission	ALSTOM	In progress

Progress for the Quarter

A draft of proposed new basic thickness rules for Section I of the Boiler Code were distributed to Task 8 participants and to Section I, Sub Committee Design of the ASME Boiler Code, for preliminary comments.

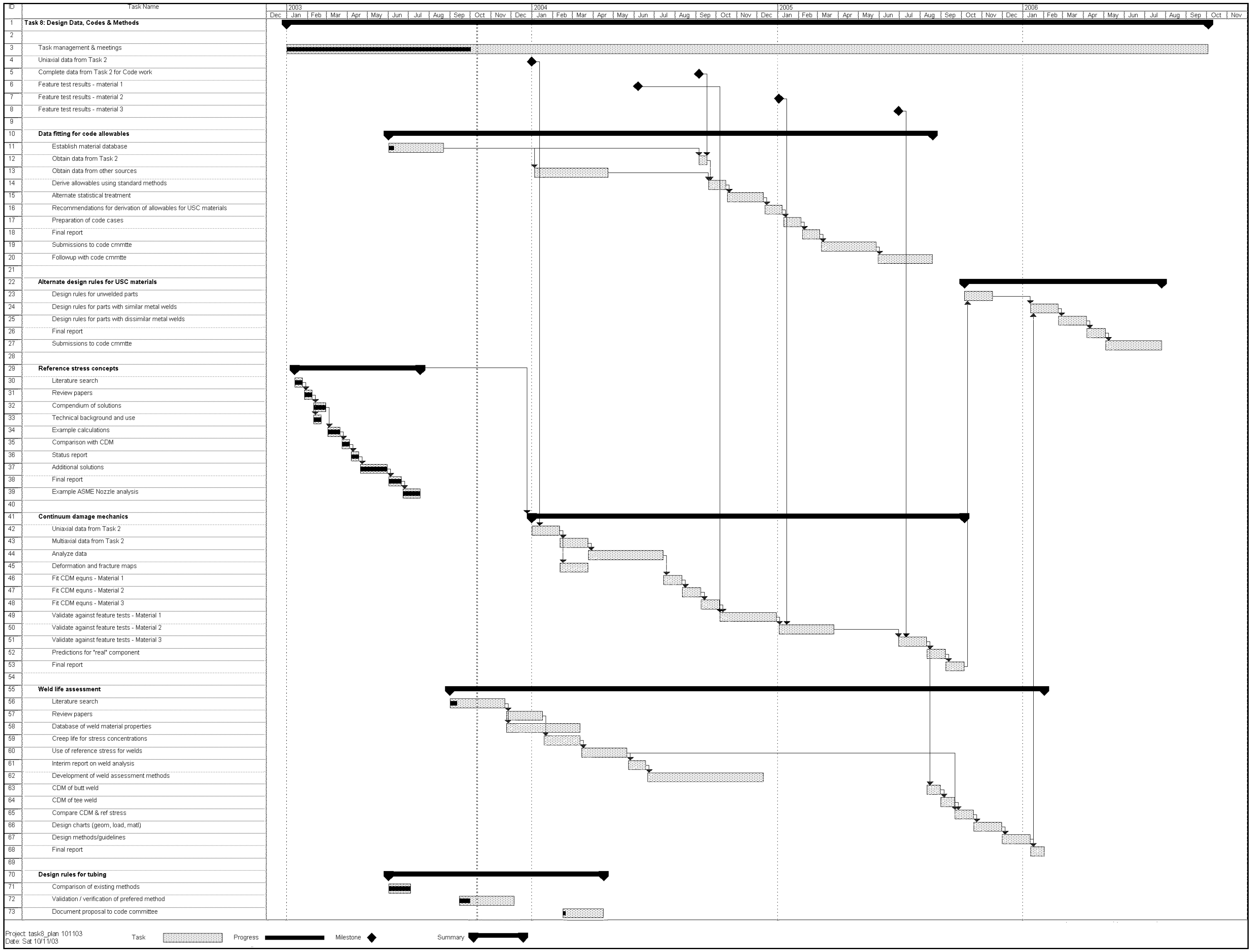
Concerns

None.

Plans for the Next Quarter

Complete Code Case and submit to code committee.

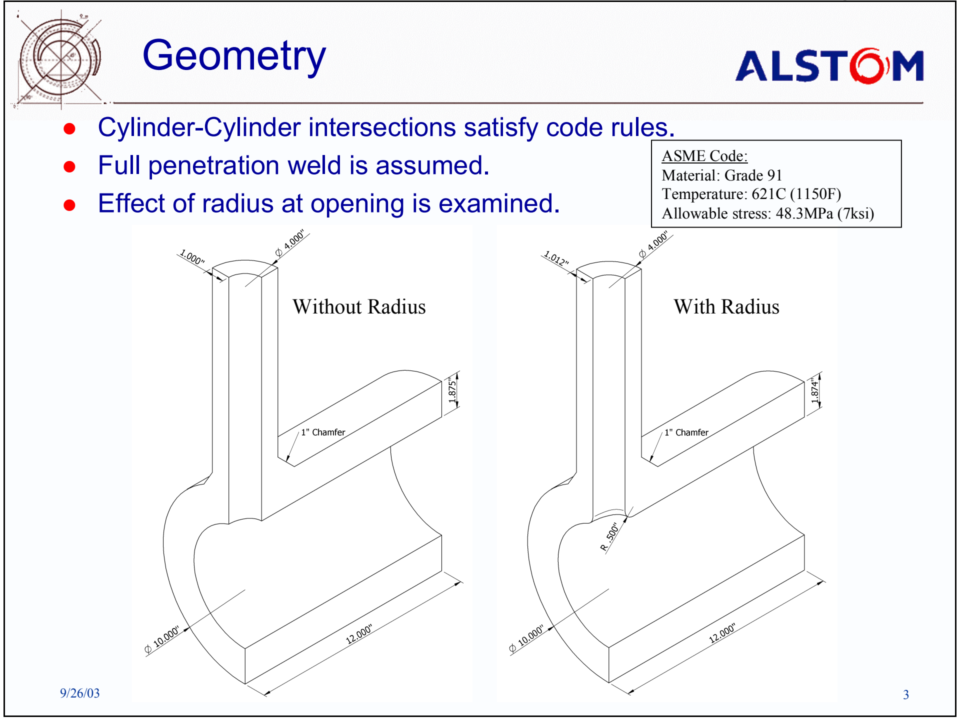
Appendix A: Project Plan with Progress Identified



ID	Task Name
1	**Task 8: Design Data, Codes & Methods**
2	
3	Task management & meetings
4	Uniaxial data from Task 2
5	Complete data from Task 2 for Code work
6	Feature test results - material 1
7	Feature test results - material 2
8	Feature test results - material 3
9	
10	**Data fitting for code allowables**
11	Establish material database
12	Obtain data from Task 2
13	Obtain data from other sources
14	Derive allowables using standard methods
15	Alternate statistical treatment
16	Recommendations for derivation of allowables for USC materials
17	Preparation of code cases
18	Final report
19	Submissions to code cmmtte
20	Followup with code cmmtte
21	
22	**Alternate design rules for USC materials**
23	Design rules for unwelded parts
24	Design rules for parts with similar metal welds
25	Design rules for parts with dissimilar metal welds
26	Final report
27	Submissions to code cmmtte
28	
29	**Reference stress concepts**
30	Literature search
31	Review papers
32	Compendium of solutions
33	Technical background and use
34	Example calculations
35	Comparison with CDM
36	Status report
37	Additional solutions
38	Final report
39	Example ASME Nozzle analysis
40	
41	**Continuum damage mechanics**
42	Uniaxial data from Task 2
43	Multiaxial data from Task 2
44	Analyze data
45	Deformation and fracture maps
46	Fit CDM equns - Material 1
47	Fit CDM equns - Material 2
48	Fit CDM equns - Material 3
49	Validate against feature tests - Material 1
50	Validate against feature tests - Material 2
51	Validate against feature tests - Material 3
52	Predictions for "real" component
53	Final report
54	
55	**Weld life assessment**
56	Literature search
57	Review papers
58	Database of weld material properties
59	Creep life for stress concentrations
60	Use of reference stress for welds
61	Interim report on weld analysis
62	Development of weld assessment methods
63	CDM of butt weld
64	CDM of tee weld
65	Compare CDM & ref stress
66	Design charts (geom, load, matl)
67	Design methods/guidelines
68	Final report
69	
70	**Design rules for tubing**
71	Comparison of existing methods
72	Validation / verification of prefered method
73	Document proposal to code committee

Project: task8_plan 101103
Date: Sat 10/11/03

Appendix B: Sample Slides from ASME Nozzle Analysis



Geometry

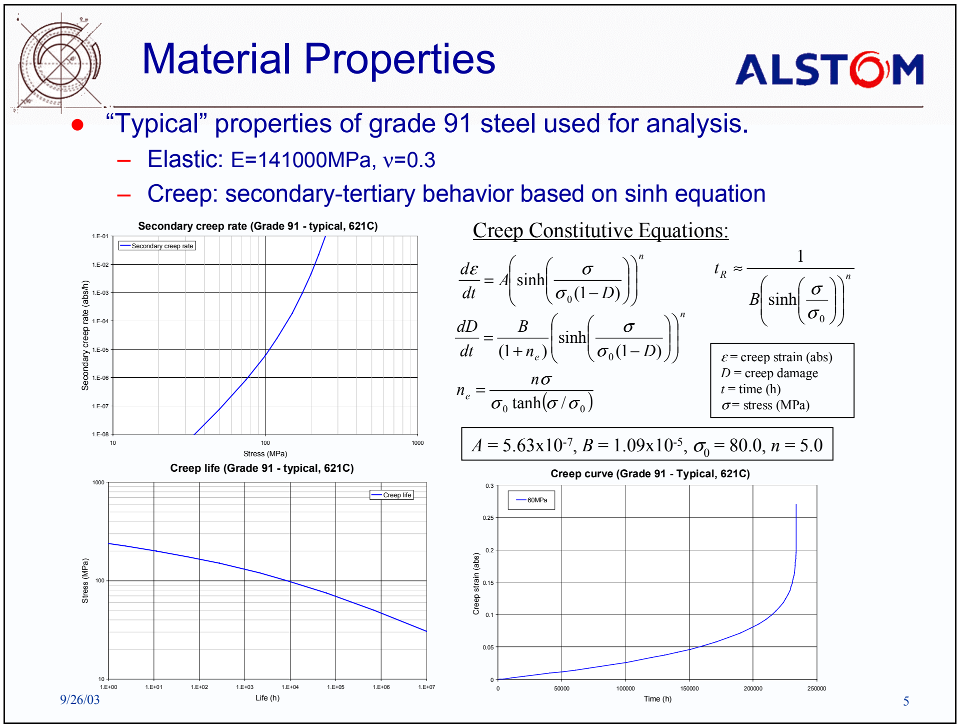
- Cylinder-Cylinder intersections satisfy code rules.
- Full penetration weld is assumed.
- Effect of radius at opening is examined.

ASME Code:
Material: Grade 91
Temperature: 621C (1150F)
Allowable stress: 48.3MPa (7ksi)

Without Radius

With Radius

9/26/03



Material Properties

- "Typical" properties of grade 91 steel used for analysis.
  - Elastic: E=141000MPa, ν=0.3
  - Creep: secondary-tertiary behavior based on sinh equation

Secondary creep rate (Grade 91 - typical, 621C)

Creep life (Grade 91 - typical, 621C)

Creep Constitutive Equations:

$$\frac{d\varepsilon}{dt} = A\left(\sinh\left(\frac{\sigma}{\sigma_0(1-D)}\right)\right)^n \qquad t_R \approx \frac{1}{B\left(\sinh\left(\frac{\sigma}{\sigma_0}\right)\right)^n}$$

$$\frac{dD}{dt} = \frac{B}{(1+n_e)}\left(\sinh\left(\frac{\sigma}{\sigma_0(1-D)}\right)\right)^n$$

$$n_e = \frac{n\sigma}{\sigma_0 \tanh(\sigma/\sigma_0)}$$

ε = creep strain (abs)
D = creep damage
t = time (h)
σ = stress (MPa)

$$A = 5.63\text{x}10^{-7},\ B = 1.09\text{x}10^{-5},\ \sigma_0 = 80.0,\ n = 5.0$$

Creep curve (Grade 91 - Typical, 621C)

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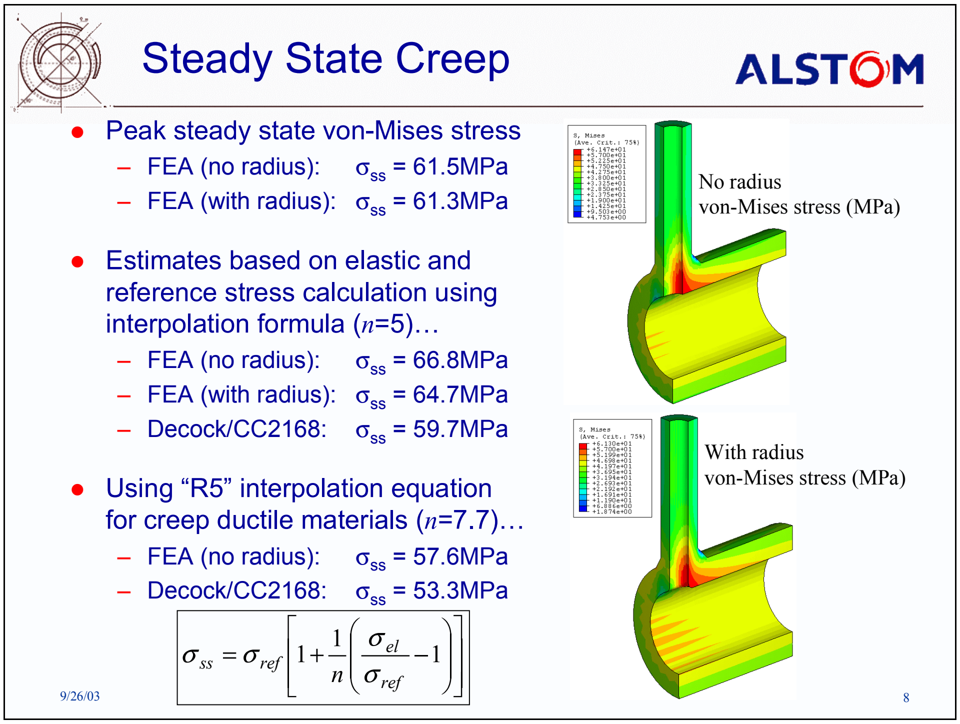

Steady State Creep

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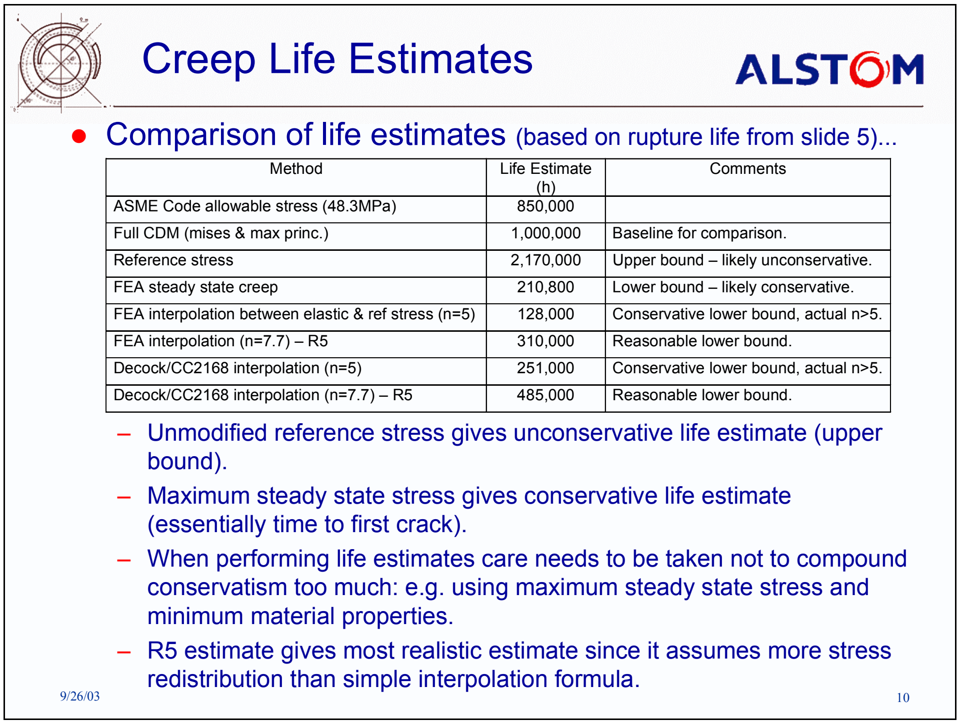
- Peak steady state von-Mises stress
  - FEA (no radius): σ_{ss} = 61.5MPa
  - FEA (with radius): σ_{ss} = 61.3MPa
- Estimates based on elastic and reference stress calculation using interpolation formula (n=5)…
  - FEA (no radius): σ_{ss} = 66.8MPa
  - FEA (with radius): σ_{ss} = 64.7MPa
  - Decock/CC2168: σ_{ss} = 59.7MPa
- Using “R5” interpolation equation for creep ductile materials (n=7.7)…
  - FEA (no radius): σ_{ss} = 57.6MPa
  - Decock/CC2168: σ_{ss} = 53.3MPa

$$\sigma_{ss} = \sigma_{ref}\left[1 + \frac{1}{n}\left(\frac{\sigma_{el}}{\sigma_{ref}} - 1\right)\right]$$

No radius
von-Mises stress (MPa)

With radius
von-Mises stress (MPa)



Creep Life Estimates

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- Comparison of life estimates (based on rupture life from slide 5)...

Method	Life Estimate (h)	Comments
ASME Code allowable stress (48.3MPa)	850,000	
Full CDM (mises & max princ.)	1,000,000	Baseline for comparison.
Reference stress	2,170,000	Upper bound – likely unconservative.
FEA steady state creep	210,800	Lower bound – likely conservative.
FEA interpolation between elastic & ref stress (n=5)	128,000	Conservative lower bound, actual n>5.
FEA interpolation (n=7.7) – R5	310,000	Reasonable lower bound.
Decock/CC2168 interpolation (n=5)	251,000	Conservative lower bound, actual n>5.
Decock/CC2168 interpolation (n=7.7) – R5	485,000	Reasonable lower bound.

- Unmodified reference stress gives unconservative life estimate (upper bound).
- Maximum steady state stress gives conservative life estimate (essentially time to first crack).
- When performing life estimates care needs to be taken not to compound conservatism too much: e.g. using maximum steady state stress and minimum material properties.
- R5 estimate gives most realistic estimate since it assumes more stress redistribution than simple interpolation formula.