Metals and Ceramics Division

CRADA FINAL REPORT
FOR CRADA NO. ORNL00-0598

SAFE USE LIMITS FOR ADVANCED FERRITIC STEELS IN ULTRA-SUPERCRITICAL POWER BOILERS

Michael Gold
James Tanzosh
Babcock & Wilcox Company.

R. W. Swindeman, P. J. Maziasz, and M. L. Santella
Oak Ridge National Laboratory

Prepared by
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
Managed by
UT-BATTELLE, LLC
For the
U.S. Department of Energy
Under contract DE-AC05-00OR22725

This research was supported through a CRADA with McDermott Technologies, Inc., sponsored by U.S. Department of Energy, Associate Secretary for Office of Fossil Energy Advanced Research under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

Abstract

In 2000, a Cooperative Research and Development Agreement (CRADA) was undertaken between the Oak Ridge National Laboratory (ORNL) and the Babcock & Wilcox Company to examine the databases for advanced ferritic steels and determine the safe limits for operation in supercritical steam power boilers. The materials of interest included the vanadium-modified 9-12% Cr steels with 1-2% Mo or W. The first task involved a review of pertinent information and the down-selection of a steel of special interest. The long-time database for 9Cr-1Mo-V steel was found to be most satisfactory for the examinations, and this steel was taken to be representative of the group. The second task involved the collection of aged and service exposed samples for metallurgical and mechanical testing. Here, aged samples to 75,000 hours, laboratory-tested samples to 83,000 hours, and service-exposed sample with up to 143,000 hours exposure were collected. The third task involved mechanical testing of exposed samples. Creep-rupture testing to long times was undertaken. Variable stress and temperature testing was included. Results were compared against the prediction of damage models. These models seemed to be adequate for life prediction. The fourth task involved the metallurgical examination of exposed specimens. Changes in microstructure were compared against published information on the evolution of microstructures in 9Cr-Mo-V steels and the results were found to be consistent with expectations. The fifth task involved a survey of steam and fireside corrosion. Data from the service-exposed tubing was examined, and a literature survey was undertaken as part of an activity in support of ultra-supercritical steam boiler technology. The corrosion study indicated some concerns about long-time fireside corrosion and suggested temperature limits were needed for corrosive coal ash conditions.

Objectives

The objectives of the Cooperative Research and Development Agreement (CRADA) between UT-Battelle, LLC, (Contractor) and Babcock & Wilcox Technologies, Inc. (Participant) was to use state-of-the-art methods of material evaluation and analysis to determine the safe use limits for advanced ferritic steels that are candidates for construction of fossil power supercritical and ultra-supercritical boiler superheater components. It was recognized a priori that these highly complex steels undergo significant microstructural alteration, steam corrosion, and fireside wastage at the service conditions for which they are envisioned, but no practical alternative alloys are available. Since the development of optimized compositions, fabrication technologies, and operating limits have a major impact on the projection of capital and operating costs for the advanced steam cycle power plants, an accurate assessment based on knowledge of long-time material performance was judged to be essential to the development process.

Benefits

The CRADA was expected to lend credibility to a technology that significantly increases in the efficiency of fossil fuels combustion with concomitant reductions in CO_2 emissions. Increasing the temperature of operation for advanced ferritic steel structural components is expected to increase plant efficiencies to substantially over 40% for pulverized coal combustion. If the life-prediction methodology can be shown to reliably establish the operating limits, full use can be made of the potential of third and fourth generation ferritic steels. Plants can be designed that lower heat rates and raise efficiencies to well above 45%.

Work Performed

The scope of the CRADA encompassed both analytical and experimental work organized into five tasks. The five tasks comprised Phase 1 that covered the entire period of the 2-year CRADA effort. At the close of Phase 1, an evaluation was made of the need to extend the CRADA to Phase II, which involved additional materials and longer testing times.

Task 1 - Information Review

A detailed program plan was developed that consisted of: (1) The selection 9Cr-1Mo-V (P91, T91) steel as the principal focus for the work [Other steels such as 9Cr-1.5W-V (P92, T92), 12Cr-1.5W-V (P122, T122), 12Cr-2W-V (HCM12), 9Cr-1W-V (E911), and 2 1/4Cr-W-V (T23, P23)] were retained an a second priority basis; (2) The collection of high-temperature design data for grade 91; (3) The review of published evaluations bearing on the issue of long-time temperature limits; (4) The identification of critical metallurgical degradation mechanisms; and (5) The review of steam and fireside corrosion experience. Some aspects of the Task 1 activity are included in a recent publication [1].

Task 2 - Sample Collection and Studies

Creep-rupture data for plate, tubing, and piping products were collected. Samples included three heats of plate materials that were laboratory-aged to as long as 75,000 hours at five temperatures. These conditions are shown in Table 1. Aging temperatures ranged to as high as 704˚C. Another group of samples was from discontinued laboratory tests. These are listed in Table 2. Here, it may be seen that exposure times extended to beyond 100,000 hours in some cases although the temperatures are mostly 538˚C and below. A third group of test samples were taken from tubing removed after long-time service in two supercritical power boilers. The service times included 30,000 hours, 116,000 hours and 143,000 hours.

Table 1. Range of temperatures and times covered by aging three heats of 9Cr-1Mo-V steel

TEMPERATURE deg C	5,000 h	10,000 h	25,000 h	50,000 h	75,000 h
482	A,C	A,C	A,C	C	C
538	A,C	A,C	A,C	C	C
593	A,C	A,C	C	C	C
649	A,C	A,B,C	A,B,C	B,C	B,C
704	A,C	A,B,C	B,C		

Note: A, B, C denote three different heats

Table 2. Specimens from discontinued laboratory tests

Test No.	Product	Heat Code	Condition	Temp. °C	Stress ksi	Time h
22502	wrought	148	nt	538	28	100495
24079	wrought	176	25k/593C	593	16	37508
24357	wrought	176	25k/538C	538	30	32212
24073	wrought	394	25k/593C	593	16	37892
20824		53494	nt	538	30	6258
24752	wrought	176	nt	482	40	84147
24577	**wrought**	**394**	**nt**	**538**	**24**	**83803**
24359	wrought	176	25k/538	538	27	32109
25409	weld	pc110	760pwht	538	25.5	16585
25604	weld	pc111	760pwht	593	17	10727
23507	cast	69	as-cast	482	35	59408
24007	cast	603	as-cast	538	20	40051
24363	weld	pc110	760pwht	538	26	80256
24279	weld	pc129	732pwht	538	30	82058
25403	weld	pc110	760pwht	538	27	16746
24899	wrought	148	nt	538	24	82060
21822	wrought	394	nt	427	60	132539
24772	wrought	148	nt	482	40	83126
25410	weld	pc111	760pwht	538	26	16439
24351	wrought	394	25k/538C	538	30	32460
23698	wrought	394	nt	427	55	106523
24820	**wrought**	**383**	**nt**	**538**	**24**	**82697**
24749	wrought	394	nt	482	40	83491
24995	wrought	pc163	760pwht	593	11	79009
25535	weld	pc111	760pwht	538	24	13701
20842	wrought	5349	nt	538	26	132647
27403	**wrought**	**383**	**nt**	**538**	**30**	**40220**
24847	**wrought**	**176**	**nt**	**538**	**24**	**82860**
24118		582	nt	593	16	96544
25401	weld	pc111	760pwht	538	28	16941
27386	**wrought**	**383**	**qt**	**538**	**30**	**40871**

Table 3. Service conditions for superheater tubing

BOILER	STEAM TEMP.(C)	PRESSURE (Mpa)	SERVICE TIME (h)
A	540	14	30,500
B	567	12.7	116,000
B	567	12.7	143,000

Task 3 - Creep-Rupture Evaluations

The historic database for 9Cr-1Mo-V steel was collected and analyzed. Creep rupture data, for example, were collected and correlated on the basis of the Larson-Miller time-temperature parameter (LMP). The results are summarized in Fig. 1. Here, the stress is plotted against the parameter LMP value for nearly 1000 test data produced in the U.S., Japan, and Europe. The parametric constant was taken as 30. The overall trend of the data suggests a downward curvature with increasing LMP. The concern regarding operating limits for 9Cr-1Mo-V steel includes the impact of the rapid fall off in strength at the highest temperatures or longest times. Data at the upper limit for 9Cr-1Mo-V steel are relatively few. At 593˚C the allowable design stress is 70 MPa (10.3 ksi) for section thicknesses of 75 mm (3 inches) or less. This stress is near the limit of the database. At 649˚C the allowable stress is 30 MPa (4.3 ksi). At this stress, there are few data to support the extrapolated stress. To produce data at the allowable stress limit, laboratory testing must be performed at 704˚C where oxidation effects are a problem.

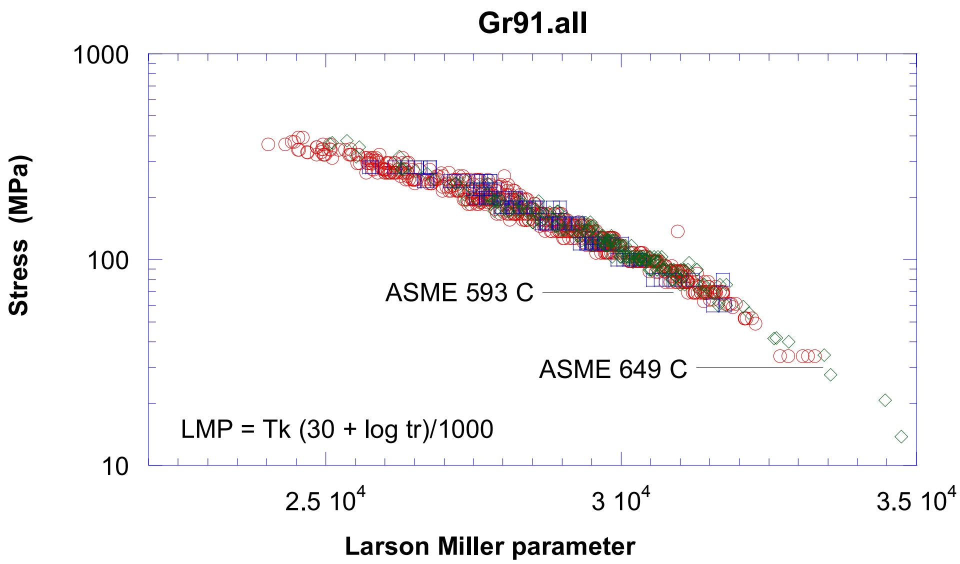

Fig. 1. Stress versus Larson Miller parameter for the 9Cr-1Mo-V steel database

Thermal aging for long times at the higher temperatures was expected to simulated long-time service conditions at lower temperatures. Thus, 10,000 to 25,000 hours of thermal aging at 649˚C was judged to be representative of very long-time service at 593˚C and similar times at 704˚C were judged to be representative of very long-times at 649˚C. Creep-rupture testing of materials aged at conditions listed in Table 1 produced shorter rupture lives than as-normalized and tempered (NT) materials but no test data indicated that the strength of long-time aged materials fell below the allowable strengths for 9Cr-1Mo-V steel for the test temperature. Typical trends are shown in Fig. 2. The plot includes some of the more than 90 creep-rupture tests performed on aged material. The results are compared to the stress allowables from ASME Sect. II, Part D. It is clear that more testing is needed at stress below 100 MPa, but the CRADA ended before this testing could be completed. Some aspects of the aging work were presented in 2000 [2].

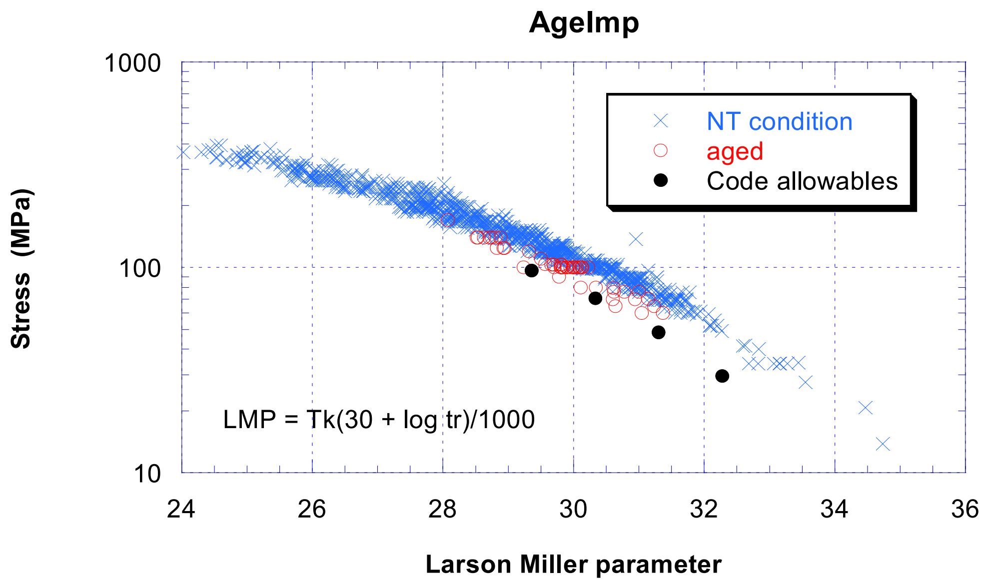

Fig. 2. Comparison of rupture data for aged material with the as-NT database and ASME allowables on the bases of the Larson Miller parameter

Several specimens from the list in Table 2 were tested at 600˚C and 100 MPa. The specimens are identified by the bold printed lines in the table. All exposures were at a relatively low temperature, 538˚C, but long times were involved. For the test condition of 600˚C and 100 MPa, an unexposed specimen would survive more than 30,000 hours. Significant damage was judged to be present in some of the exposed specimens and this damage would produce shorter life. No specimens failed at the time the CRADA ended.

Specimens from the service-exposed boiler tubing were tested at a variety of stresses and temperatures ranging from 550 to 700°C. Stresses were in the range of 80 to 170 MPa. Similar to the behavior of the thermally aged specimens, the creep rupture life was reduced by service exposure. Generally, the specimens tested at the higher temperatures showed less loss in life than specimens tested at the lower range of temperatures. Again, the long-time, low stress testing was not completed before the CRADA ended.

Regardless of aging, prior creep, or service exposure conditions, the creep rate versus rupture life correlation was identical. This correlation, known as the Monkman-Grant plot, is shown in Fig. 3. If this plot holds for the high-temperature, low-stress condition then use can be made in estimating life from the shorter time testing required to establish the minimum creep rate. Unfortunately, one can only be sure that the correlation holds by actually running the long-time rupture test.

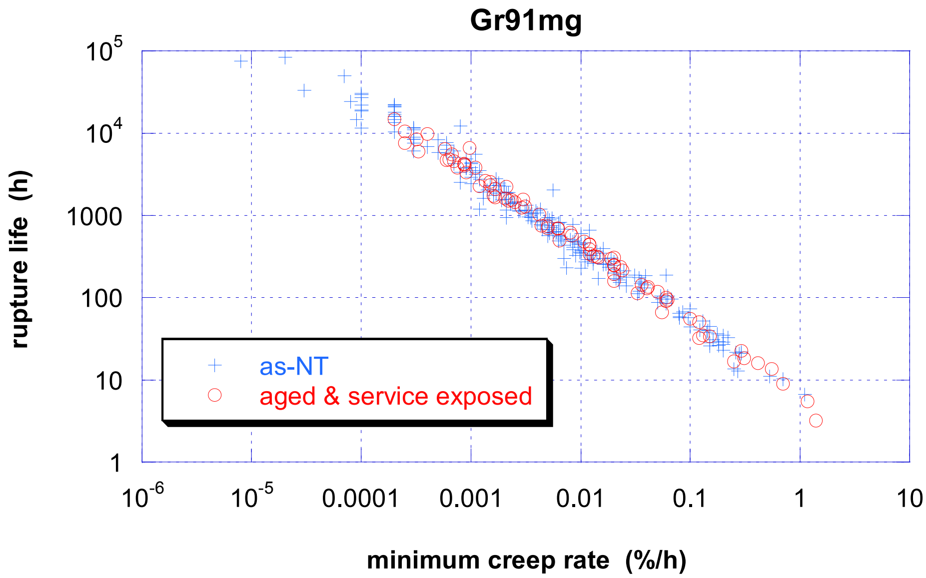

Fig. 3. Comparison of the Monkman-Grant trend for as-NT, aged, and service exposed materials

As the CRADA progressed, the performance of weldments in the advanced ferritic steels took on importance. A number of issues arose that related to welding technology and the subsequent long-time performance of welded components. The Participant delivered a thick-section weldment to the contractor. This material was used to examine a number of important issues. Included were: (1) the effect of nickel plus manganese content on the critical transformation temperatures such as the martensitic start and finish and the A_{c1} transformation temperature, (2) the effect of retained austenitic on the performance after post-weld heat treatment, (3) the effect of post weld heat treatment temperature on creep-rupture, and (4) the effect of renormalization on the creep rupture of weldments. Some aspects of this work were included in a recent publication [3].

Task 4 - Metallurgical Investigation

Metallurgical investigation of aged, mechanically tested, and service-exposed samples were undertaken. Optical microscopy and scanning electron microscopy (SEM) were performed. General features that were examined included cracking modes, grain stability, and precipitate characteristics. Transmission electron microscopy (TEM) and analytical electron microscopy (AEM) were performed. The investigation produced results that were consistent with previously published results. The long-time exposure at high temperature results in evolution of microstructure to a softer, less creep-resistant condition.

Task 5 - Oxidation and Corrosion Behavior Study

The fireside and steamside corrosion of the exposed superheater tubing were compared to literature models and found to be more-or-less consistent with these models (3). Literature reviews, plant experiences, and results from parallel studies that produced experimental results were incorporated into an analysis and assessment of the operating limits imposed by corrosion.

These results were incorporated into an assessment performed a part of the ultra-supercritical steam boiler project supported by the DOE (4).

Inventions

The 9Cr-1Mo-V steel was developed under support by the U.S. Department of Energy (DOE) for use on nuclear and fossil energy programs. A second steel, 9Cr-W-V-Ta, was also developed under DOE support for application in fusion energy programs. No new inventions resulted from the work on this CRADA.

Commercialization Possibilities

The steels investigated in this CRADA are being used extensively in the U.S. for both new and replacement functions. Further extension of the application for these steels to longer times or higher will depend on the results of collaborative efforts now underway.

Plans for Future Collaboration

Collaboration is underway between Babcock & Wilcox, ORNL and a number of other companies to continue the research on the service limits for the advanced ferritic steels. Some of the testing initiated under this CRADA will be continued and expanded to resolve the issues important to the production of more efficient power generation.

Conclusions

The upper temperature limit for 9Cr-1Mo-V steel is more determined by steamside and fireside corrosion than by long-time creep rupture strength. Although the strength degrades with continued exposure there is no evidence that the long-time strength falls below the stress allowables currently listed in ASME Sect. II, Part D. However, further evaluation of creep behavior at low stress is needed to fully understand the damage accumulation mechanisms at conditions typical of component operation. This is especially true for components that are expected to operate at 600°C and above.

Acknowledgements

Much of the material collected and aging was undertaken under the supervision of C. R. Brinkman and V. K. Sikka of the Metals and Ceramics Division. The assistance of R. R. Judkins, Manager of Fossil Energy Programs at ORNL, and F. V. Damiano of UT-Battelle, LLC contracts is appreciated.

References

1. R. W. Swindeman, M. L. Santella, P. J. Maziasz, B. W. Roberts, and K. Coleman, "Issues in Replacing Cr-Mo Steels and Stainless Steels with 9Cr-1Mo-V Steel," paper presented at the 7th International Conference on the Operation of Pressure Equipment, Carlton Hotel, Sydney, Australia, April 2-4, 2003.

2. R. W. Swindeman, P. J. Maziasz, and C. R. Brinkman, "Aging Effects on the Creep-Rupture of 9Cr-1Mo-V Steel," paper published in the proceedings of the 2000 International Joint Power Generation Conference, Miami Beach, Florida, July 23-26, 2000

3. M. L. Santella, R. W. Swindeman, R. W. Reed, and J. M. Tanzosh, "Martensite Transformation, Microstructure, and Creep Strength of 9Cr-1Mo-V Steel Weld Metal," pp. 713-718 in Proceedings of the 6th International Conference on Trends in Welding Research, ASM International, Materials Park, Ohio, 2003.

4. J. Sarver, R. Viswanathan, and S. Mohamed, Boiler Materials for Ultra Supercritical Coal Power Plants-Task 3, Steamside Oxidation of Materials, NETL/DOE, 2003, USC T-5, Electric Power Research Institute, Palo Alto, CA 94304 (June 2003).

INTERNAL DISTRIBUTION

1. P. A. Carpenter, 4500N, 6269
2. P. J. Hadley, 4500S, 6161
3. D. R. Hamrin, 6011, 6254
4. R. R. Judkins, 4508, 6084
5. E. Lara-Curzio, 4515, 6069
6. P. J. Maziasz, 4500S, 6115
7. T. M. Rosseel, 4500S, 6161
8. M. L. Santella, 4508, 6096
9. R. W. Swindeman, 4500S, 6155
10. K. M. Wilson, 111B UNV, 6499
11. I. G. Wright, 4500S, 6156
12. DOE, WFO, 1000, 6396

EXTERNAL DISTRIBUTION

13. Fred Glaser, Portfolio Manager, Department of Energy, Fossil Energy, Office of Advanced Research, FE-72, 19901 Germantown Road, Germantown, MD 20585
14. M. Gold, Gold Metallurgical Services, LLC, 588 Eddy Lane, North Benton, OH 44449-9735
15. V. Udaya S. Rao, U.S. Department of Energy, National Energy Technology Laboratory (NETL-PGH), 626 Cochrans Mill Road, Pittsburgh, PA 15236-0940
16. Richard B. Read, U. S. Department of Energy, National Energy Technology Laboratory, (NETL-PGH), 626 Cochrans Mill Road, Pittsburgh, PA 15236-0940
17. Robert R. Romanowsky, Jr., U.S. Department of Energy, National Energy Technology Laboratory (NETL-MGN), 3610 Collins Ferry Road, Morgantown, WV 26505-0880
18. Marvin I. Singer, 4G-052/FORS, U.S. Department of Energy, Headquarters, Forrestal, 1000 Independence Avenue, S.W., Washington, DC 20585
19. J. M. Tanzosh, Babcock & Wilcox, 20 Van Buren Avenue, P. O. Box 351, BVS03B, Barberton, OH 44203-3585