Heat-Resistant Advanced 9% Cr Steel for Fossil Energy Power Generation

J.A. Hawk and P.D. Jablonski

National Energy Technology Laboratory, U.S. Department of Energy
1450 Queen Avenue SW, Albany, OR, USA
Jeffrey.Hawk@netl.doe.gov, Paul.Jablonski@netl.doe.gov

ABSTRACT

NETL has designed and manufactured a heat-resistant 9% Cr steel for use in coal-fired power plants. Creep testing has shown the NETL steel, designated CPJ7, has longer life than existing commercial heat-resistant steels at the same temperature. This longer life could translate into an approximately 50°F improvement in operating temperature, depending upon the power plant component, which would improve overall plant efficiency. The NETL CPJ7 steel was made into both fully wrought plate as well as laboratory-scale castings.

Keywords: 9% Cr steel, heat resistant steel, tensile properties, creep capability, wrought, cast

1 INTRODUCTION

Martensitic and/or ferritic steels containing chromium (Cr) form the backbone of the U.S. fleet of coal-fired power plants. In general, these alloy classes are inexpensive to produce and can be recycled, which makes them favorable for use as boiler and steam turbine components such as tubing, piping, headers, rotors, and buckets. Since many power plant components are very large and/or very thick (up to 100 mm for some components such as steam headers), the thermal stresses that arise at start-up and when swing-loading electricity production at peak times must be minimized. The enhanced thermal conductivity and lower thermal expansion coefficient of martensitic and ferritic alloys makes them a more favorable option than austenitic stainless steels, especially when coupled with the cost difference between the alloy classes.

For coal-fired power plants in the United States that operate at or below 570°C, CrMoV, NiCrMoV, and steels with less than 5% Cr (henceforth all compositions are given in weight percent unless otherwise noted) make up the majority, in tonnage, of steam turbine and boiler components. For hotter sections of the boiler and for the majority of the steam turbine components, 9–12% Cr steels are used because of their superior strength and creep performance. Currently, the approximate maximum use temperature for 9–12% Cr steels is 620°C because long-term microstructural instabilities preclude maintaining creep strength at temperatures up to 650°C for times greater than or equal to 100,000 hours (note that very few power plants operate at this temperature.)

Reducing the cost of construction, increasing efficiency, or both, will make coal-fired power plants more attractive. A tempered martensitic ferritic steel alloy for use at 650°C would significantly improve power plant efficiency at a fraction of the cost required to build a 700°C power plant. In addition, a power plant constructed from tempered martensitic ferritics capable of operation at 650°C would obviate the need for a 700°C power plant and would enable research efforts to be focused on developing a 760°C advanced ultra-supercritical plant, which is the next step up in efficiency improvement and will require precipitation strengthened nickel-based superalloys.

Research in improving the temperature and pressure capability of power plant steels has been active since the 1950s. Metallurgical advancements in the design and manufacture of steels have been a driving force in raising steam conditions in power plants from subcritical to ultra-supercritical. In 1968 Fujita [1] developed TAF steel, which nearly meets today's creep lifetime requirement at 650°C. A major feature of the TAF steel's creep resistance was accounted for by the high boron (B) level in the base steel. Even though it exhibited exemplary creep performance, the TAF steel proved extremely difficult to fabricate and to weld, and these aspects point to a global issue with these alloys. Even if the creep strength, oxidation, and corrosion requirements were met, TAF steel would still not be a useful product for power plant applications. These materials must be fabricable on a multiple tonnage scale to produce components, and they must be weldable and ultrasonically inspectable.

The goal of this NETL alloy development program is to produce a tempered martensitic ferritic steel capable of use at temperatures up to 650°C for 100,000 hours or greater. To achieve this goal, it is necessary to understand high-temperature strengthening mechanisms, and how to preserve these mechanisms for the required time frames through appropriate microstructure design and control.

The alloy design concept taken for this work was to eliminate the sources of microstructural instability identified in the tempered martensitic ferritic steels, such as Z-phase, Laves phase, and coarsening of the MX and $M_{23}C_6$ precipitates.

A number of alloy chemistries have been investigated in this effort. One chemistry variant emerged from which a patent application was submitted and a patent granted. To rank and compare the effectiveness of this alloy design concept, herein designated CPJ7, the microstructure and mechanical properties of this alloy were characterized, and then compared against commercial 9–12%Cr steels. A summary of these comparisons are presented here.

2 ALLOY DESIGN BASIS & EXECUTION

Computational thermodynamic modeling was used to screen possible alloy compositions based upon the predicted equilibrium phases. Nominal alloy compositions, including CPJ7, were formulated from commercial purity raw materials and compacted prior to Vacuum Induction Melting (VIM). For each nominal composition, a 6.8 kg ingot was melted and cast into a cylindrical graphite mold that employed a zirconia wash coat. The actual composition of each alloy was determined using X-ray Fluorescence, LECO spectroscopy for C, O, N, and S, and Inductively Coupled Plasma Optical Emission Spectroscopy for B. After hot top removal and surface conditioning, each ingot was given a computationally optimized homogenization heat treatment prior to fabrication. Fabrication consisted of hot forging, followed by hot rolling operations at 1000°C to convert each ingot into fully wrought plate approximately 10 mm thick.

To develop a tempered martensitic microstructure for subsequent characterization and property evaluation, a normalizing study was performed at various temperatures between 1000–1200°C, followed by tempering at 700°C. The normalized and tempered microstructures produced in CPJ7 using 1150°C/30m/AC followed by 700°C/1h/AC (i.e., N&T) were subsequently tested to determine tensile mechanical strength at temperature and creep capacility. Tensile properties were determined at NETL from room temperature up to, and including, 650°C. Constant-load creep testing in air at 650°C was performed at NETL for stresses between 30 ksi and 15 ksi.

3 ALLOY DESIGN RATIONALE

Alloy CPJ7 has a nominal composition of Fe-10Cr-1.25Mo-0.5W-1.5Co-0.2V-0.05Nb-0.02N-0.15C-0.01B-0.5Mn-0.3Si [1]. The selection of this nominal composition was based on thermodynamic modeling to ameliorate sources of microstructural instability such as Z-phase, Laves phase, and coarsening of the MX and $M_{23}C_6$ precipitates.

A Cr content of 10% was chosen for this alloy to balance the effect Cr has on strength and oxidation resistance. Chromium contents approaching 12% improve oxidation and corrosion resistance, but at the expense of creep strength. Increasing the Cr content also increases the driving force for Z-phase.

Cobalt rather than Ni was utilized as a solid solution strengthening element, and austenite stabilizer, becasue Co has only a moderate effect on the Ac1 temperature, it raises the Ms and Curie temperatures, and it is expected to slow diffusion processes and the consequent coarsening of precipitates [3]. It has also been suggested that Cobalt delays recovery during tempering of martensitic steels, promoting nucleation of finer secondary carbides during tempering, and slowing the coarsening of carbides, which is suggested to result from Co increasing the activity of carbon while Co itself is not soluble in alloy carbides [4].

To limit Laves phase, W was added at 0.5 weight percent as a solid solution strengthening element. Molybdenum was also used at 1.25 weight percent. This provided the optimum level of Mo+W at about 1.5.

The V and Nb contents were set to those typically found in advanced 9–12% Cr steels to produce an optimum size and volume fraction of MX precipitates.

Boron was added at a level of no more than 100 ppm to enhance the stability of the $M_{23}C_6$ precipitates, and hence stabilize subgrain structure. Atom probe results have shown that B enters the structure of the $M_{23}C_6$ carbides and B also segregates to the $M_{23}C_6$-matrix interface [4]. It has also been suggested that B has the beneficial aspect of assisting in the nucleation of VN, a mechanism dubbed “latent creep resistance” [4].

The Mn and Si contents were kept at levels sufficient to provide oxidation and corrosion resistance, while not adversely affecting other microstructural features and material properties.

The C and N contents of this alloy were kept in the typical range for 9–12% Cr steels; 0.1–0.2% for C and 0.01-0.06% for N in these alloys. A nominal C content of 0.15% was chosen to provide an appropriate amount of carbide ($M_{23}C_6$ and MC) precipitates while ensuring ease of weldability for end-use applications. A nominal N content of 0.02 wt% was chosen to facilitate MX formation while lowering the driving force for Z-phase. Since MX precipitates provide the strongest barrier to dislocation motion and recovery processes, it is imperative to incorporate as much N as possible into the alloy to get the largest volume fraction of MX precipitates, but without adding enough to favor Z-phase.

Copper and Ta were also added at low levels to CPJ7 steel to provide additional strength at elevated temperature.

4 CPJ7 MECHANICAL BEHAVIOR

Figure 1 shows a summary of the tensile yield stress and tensile strenght of CPJ7 for several laboratory-scale heats as a function of temperature. For comparison the mean curve for COST E is shown.

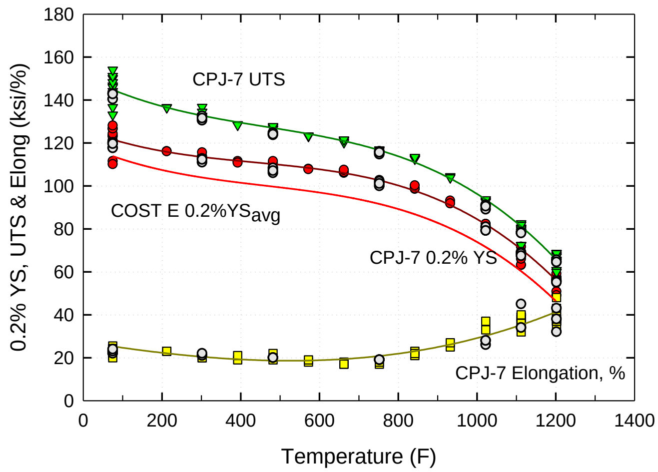

Figure 1. Several heats of CPJ7 steel showing 0.2% YS, UTS, and elongation to failure. Mean curve of 0.2% YS for COST E is shown for comparison.

Two features are readily apparent. First, the mechanical behavior of the CPJ7 steel is consistent from heat to heat. Second, the trends in YS and UTS are consistent with that seen for commercial 9% Cr steel like COST E (used for steam turbine rotors). Note: COST E is a non-B containing steel, which is similar to steels with B like COST FB2.

More striking than tensile mechanical behavior is creep life for CPJ7. Figure 2 shows isothermal rupture curves for CPJ7 and COST E.

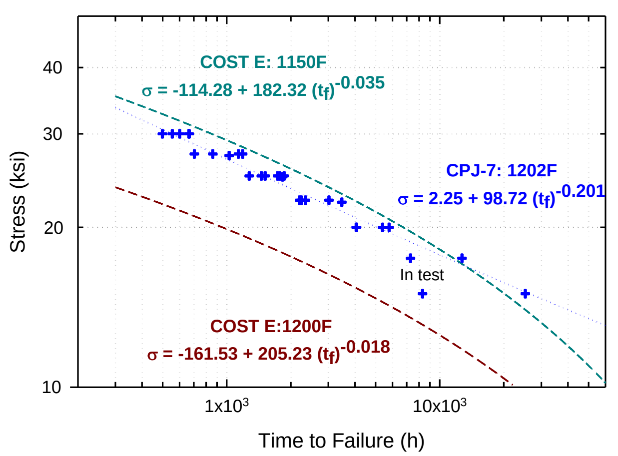

Figure 2. Isothermal rupture for CPJ7 steel versus COST E steel. (Data points on graph belong to CPJ7 steel tested at 650°C/1202°F. The data for COST E corresponds to mean curves for creep tests performed at 1150°F and 1200°F.)

Creep testing of CPJ7 steel is ongoing. However, it is clear that the overall creep capability of CPJ7 is significantly better than that for COST E. Is should be noted that COST E is a rotor steel as compared to boiler piping steels P91 and P92. The difference in creep capability between CPJ7 steels and these boiler steels is even greater in magnitude. Also, the shape of the isothermal rupture curve for CPJ7 is different from normal martensitic 9% Cr steels; CPJ7 does not yet exhibit the downward curvature at long rupture times as do typical commercial 9% Cr steels like COST E, P91, or P92. This is significant because it shows, at least through the testing performed to date (up to 25,000 hours at 650°C), a stable microstructure that is resistant to the usual detrimental effects (Laves formation, Z-phase, etc.) exhibited by this class of steels. (To be conclusive, longer terms creep tests must be performed.)

Regardless, CPJ7 shows about a 50°F (~29°C) improvement in creep life capability over COST E. That is, CPJ7 tested at 650°C has roughly the same time to rupture as COST E at 621°C.

5 CAST VARIANT OF CPJ7

The success of the wrought version of CPJ7 suggested that a cast version of the steel might also be superior to existing commercial 9% Cr steel castings used for valve chests and rotor casings. Subsequently, NETL manufactured a series of laboratory-scale castings based on the wrought version chemistry. The castings were homogenized in the same manner as the wrought version and subsequently normalized and tempered in the same way. COST CB2 was used as the commercial benchmark alloy for comparison with respect to creep capability. Figure 3 shows the tensile behavior of the two steels.

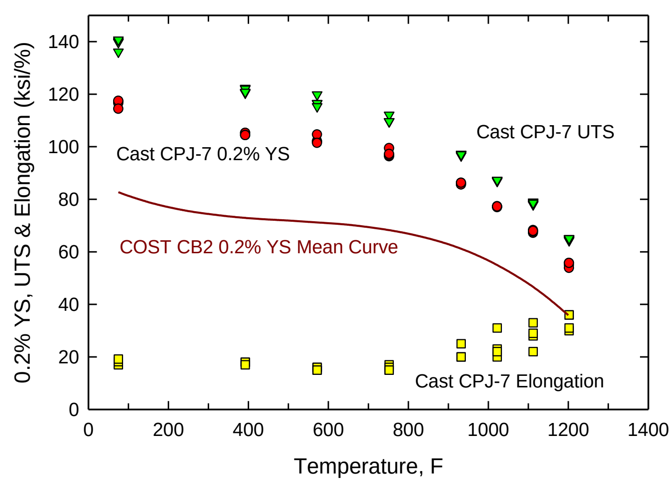

Figure 3. Cast version of CPJ7 compared against COST CB2. Although not directly compared on this graph, the tensile mechanical properties of cast CPJ7 are very similar in magnitude to the wrought version. Note the significant difference in 0.2% YS between cast CPJ7 and COST CB2.

Cast CPJ7 has very good strength while maintaining good ductility levels that were much more consistent than found in commercial castings.

However, the most significant finding was the creep behavior of the cast CPJ7 steel. Castings by their very nature, especially those that have large section thickness, have large grains compared to their wrought analogs. Large grain size is usually associated with better creep behavior. Alternatively, castings cannot be thermomechanically processed to more consistent and refined grain size, which usually leads to better ductililty. Consequently, the elongation to failure in castings is less than in the wrought version so creep life is usually less. This was expected for cast CPJ7 but not observed. Figure 4 shows the results of the creep testing to date just for cast CPJ7, while Figure 5 shows the combined data for CPJ7 as well as the mean Larson-Miller Parameter (LMP) curves for COST E and COST CB2.

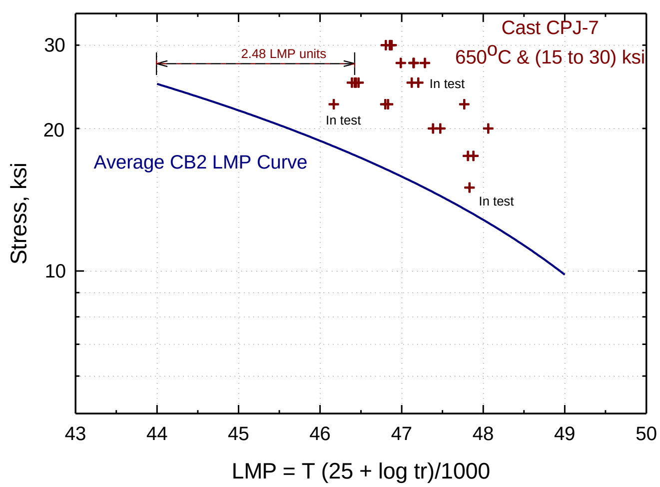

Figure 4. Comparison of creep behavior in terms of LMP for cast CPJ7 and COST CB2. Note the significant improvement in creep capability for cast CPJ7 compared to that of COST CB2, an equivalent 9% Cr casting.

Two curves for LMP and the cast CPJ7 steel should be noted. In a small laboratory casting there is the possibility of residual porosity and micro-porosity due to shrinkage during cooling. This porosity was observed in the lower value LMP but not the upper curve. Regardless, the improvement in creep capability of cast CPJ7 is significant compared to COST CB2. What is more significant is that all testing of cast CPJ7 was done at 650°C, regardless of the test stress level. It is not possible to do this with COST CB2.

Figure 5 shows the combined data for wrought and cast CPJ7 as well as the mean LMP curves for COST E and COST CB2. Significantly, the LMP curves for cast CPJ7 bracket the wrought steel curves, with the data corresponding to the creep tests showing porosity are slightly less creep capable, while the tests with material having no porosity show creep capabilities better than the wrought version. All CPJ7 creep data show better performance than the commercial alloys (note there are five ongoing tests also shown in this data set).

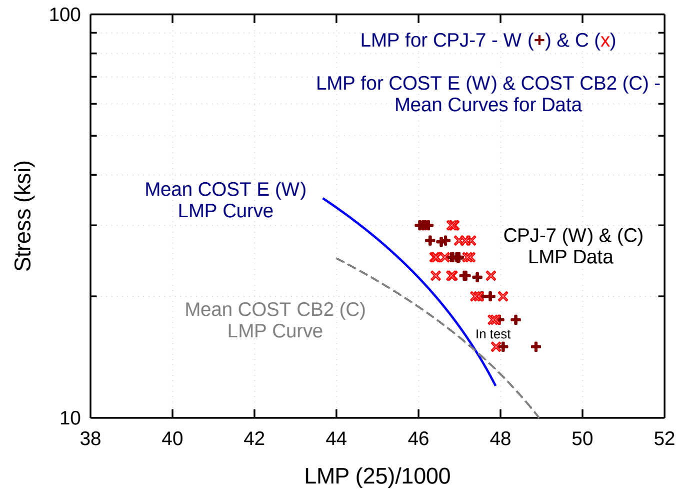

Figure 5. Data for cast and wrought CPJ7 compared against commercial alloys COST E and COST CB2.

6 SUMMARY AND PROSPECTUS

NETL has designed and manufactured a heat-resistant 9% Cr ferritic-martensitic steel with superior creep performance compared to existing commercial steels of the type. It has been made in both fully wrought plate as well as laboratory scale castings. The cast version of CPJ7 9% Cr martensitic-ferritic steel performs exceptionally well for a casting. Work is ongoing to more fully understand and develop this alloy’s potential as a replacement for existing power plant 9% Cr steels.

REFERENCES

[1] T. Fujita, *ISIJ International*, **32** (1992) 175-181 (T. Fujita, *Suppl. to Trans. Jpn. Inst. Met.*, **9** (1968) 167).
[2] J.A. Hawk, P.D. Jablonski, and C.C. Cowen, “Creep Resistant High Temperature Martensitic Steel,” *US 9,181,597 B1* (11/10/2015).
[3] V. Knezevic, J. Balun, G. Sauthoff, G. Inden, and A. Schneider, *Mater. Sci. Eng. A*, **477** (2008) 334-343.
[4] R. Viswanathan and W. Bakker, *JMEP*, **10** (2000) 81-95.
[5] J.A. Hawk, P.D. Jablonski, and C.C. Cowen, “Creep Resistant High Temperature Martensitic Steel,” *US 9,556,503 B1* (1/31/2017).