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# New Boiler Materials for High Pressure and Temperature Application


## Abstract

Energy is one of the major inputs for economic development of the developing countries. In India there is a huge demand of electricity for development. Therefore there is a great challenge for us to produce power from high capacity power plants which needs installation of high capacity super thermal power plants. This requires to generate steam at high temperatures and pressures.

Therefore we shoulddevelop such materials for boiler tubes which can withstand high temperatures and pressures. This paper includes materials used presently for supercritical boilers and future materials for high temperatures and pressures.



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## Introduction

Due to deficiency of power in country these days power generation industries are trying to generate power at high efficiency &low cost by utilizing steam at higher temperatures & high pressure. In response to such severe requirements, various types of high temperature strength materials are trying to utilize for manufacture of ultra supercritical boiler component by various countries. This paper includes materials used presently for supercritical boiler & future materials may be utilized for USC boiler at higher temperature & pressure.

### 1. Steam Generating Walls

### 1.1 Current Material

Without exception the Steam Generators tubes in the furnace walls of supercritical plants are member of wall construction. In convention supercritical plant (250 bar, 540$^0$C) the maximum temperature of the water/steam fluid in the water panel is 420$^0$ C at the outlet. Because of the high heat flow in the furnace chamber, mid wall metal is approximate 450$^0$ C on entering service. Growth and deposition of magnetite on the bore of the tubes increase the temperature difference through the walls such that, at 100,000 hours, the estimate mid-walls temperature rises to 455$^0$ C. Under such condition 1% Cr 0.5 % Mo steel has adequate mechanical properties for a 100,000 hour life. Strock Ketels use 0.5% Cr steel in the evaporator wall tubes and claim an acceptable metal temperature at the furnace outlet of 460$^0$ C. Temperature of upto 500$^0$ C can be tolerated for short periods (5 minutes) at low pressure during start up. ABB favour he uses of T11 to T22 steels and quote a maximum operating temperature of 538$^0$C. Then, C-Mn and low alloy steels can continue to be used for main steam condition of up to 580$^0$C and 290bar.

All of boiler manufacture offer some form of staged combustion to limit the nitrogen oxide emissions. In all case this implies sub-stoichiometric combustion in the lower portion of the furnace chamber such sub-stoichiometric conditions pose the danger of furnace wall fireside corrosion, which leads to very rapid thinning and hence early failure of the membrane wall tubes. ABB claim that they favor the use of T22 steel over the T11 steel because the increased chromium content offers improved oxidation resistance. However, chromium contents in excess of 25% are required before any real improvement in furnace wall corrosion rate is likely to be experienced . None of the materials proposed thus far possess sufficient corrosion resistance to withstand furnace wall fireside corrosion. For furnace wall application, bimetallic boiler tubes, such as those produced by co-extrusion, are the only tubes likely to possess the required corrosion resistance. However, the use of an austenitic outer layer for furnace wall corrosion resistance would pose tremendous difficulties with differential thermal expansion in membrane walls. Consequently, all boiler manufactures offer some means of ensuring more oxidizing conditions close to the furnace walls. ABB Steimuller and Stein Industries all use corner-fired units with, for instance, offset secondary air. Stock Ketels use a front wall fired system with the stoichiometry of the burners closest to the sidewalls set up to be more oxygen rich.

### 1.2 Materials used at 620⁰C/325bar

For USC (ULTRA SUPECRITICAL) plant of $620^0$C maximum water/steam temperature at the outlet of the water walls is approximately $475^0$C. This equates to a mid wall temperature of $497^0$C on entering service with climb. The metal temperature of the other surface may rise as high as $524^0$C in general and $539^0$Cin the Highest heat flux areas (burner Zone). The mechanical properties of conventional boiler steels are no longer adequate for this duty and more highly alloyed creep resistance materials are required. Preliminary calculations based on the allowable stress data for T23 suggest the maximum permission water/steam temperature using T23 in the water walls of supercritical plant would be $480^0$C. This should be sufficient for use in plant operating at 325bar, $620^0$C. 7CrMoVTiB10-10has slightly higher creep strength than T23 steel at temperature up to $570^0$Cwhilst above this temperature, T23 would be the preferred choice. However the long term strength values for the latter may be somewhat optimistic as they are derived from extrapolation of much shorter duration creep rupture data (~15,000hours). Further, precipitation of W-bearings. Laves phase is expected during exposure, resulting in some loss of solid solution hardening. By contrast the data for 7CrMoVTiB10-10 steel extend out to nearly 100,000hours, so that some confidence can be placed in the strength values.

Both T23 and 7CrMoVTiB10-10 are readily welded, neither requiring preheat or post- weld heat treatment. Similarly, both steels are reported to have good fabrication characteristic. However, whether either of the materials has the necessary resistance to steam oxidation for operation at such temperature remains an open question.

ALSTOM Power and Mitsui Babcock are currently considering the use of T23 for water wall application in supercritical plant. Trial panels o0f T23 and T24 have been installed in Asnaesvaerket in Denmark and Cordemains in France. Preparations are in hand for further trills 8in Weisweiler, Necker 2 and Altbatch. Vallourec and Mannesmann have just received their first commercial order for T 23 for super heater tubes in Morocco. If the ongoing test are successful then problems concerning the water walls be solved and it will be possible to operate with water/steam temperatures of $500^0$C to $520^0$C in the water walls.

### 1.3 Materials use at 650⁰C/350bar

For USC plant with steam condition above $650^0$C/350 bar, further materials improvements will be necessary to reach steam/water temperatures much above $480^0$C in water walls. In view of thermal expansion limitations in membrane wall construction, the materials of choice invariably comprise ferrite steel. In view of this, Mitsubishi heavy Industries are looking at further improving the creep strength of T23 for these applications by the addition of Re. However, considerable attention is being directed towards the 9 and 12% chromium steels such as T91/P91, X20CrMoV121 and HCM12. Notwithstanding the higher chromium contest, it should not be assumed that these steels will have adequate corrosion resistance and as they are more expensive, their use will inevitably increase constructional costs.

Full sized furnace wall panels were made from T91 and HCm 12 by a number of manufacturers for the European countries. The panels were to be completely defect-free when examined both visually and NDT. However, no manufacturer managed to complete a panel fully in compliance with the German TRD code with respect to the hardness criterion of <350Hv10 and the weld criteria not more than 150hv10, greater than the parent material, without resorting to post weld heat treatment. Efforts are being made to reducing the carbon content of these steels to ensure hardness less than the critical value of 350Hv10 in welds, without any reduction in creep strength of the materials. However masuyama expect HCM12 to be applicable to water walls because it has better weld ability than T91 and a lower susceptibility to SCC. On this basis Franklin and Henry recognized that field and discussion with local authorities will be needed before either material can be used. As part of this, ongoing development test panels of P91 and HCM12 have been built into the water walls of plant operating in Germany.

## 2. Superheater & Reheater Tubes

### 2.1 Current Materials

Super heater tubes must be designed to at temperatures some $35^0$C above the steam temperatures. For current steam temperatures up to $580^0$C, metal temperatures will be around $615^0$C and the low alloy steel tubes such as T22 may be adequate. However, not only do the advanced steam parameters for super critical plant impose higher stresses and temperatures on the super heater tubes, they also increase the potential rates of both fireside and steam side corrosion. Fireside corrosion on the other surface of super heater and reheater tubes can lead to rapid thinning and hence, subsequent premature failure by creep. Experience within the CEGB in the 1970's for plant with final steam temperatures of $565^0$C and burning coal with chlorine contents greater hen around 0.15% showed that these low alloy steels did not possess sufficient fireside corrosion resistance. Consequently, the 500 MW units required selective re-tubing with the austenitic steel T316 and T347.

If the steam temperatures are to be only moderately increased and the fireside corrosion potential is to be considered then the improved medium chromium ferrite materials steel such as P91, P92 and P122 could be considered as possible alternative to X20CrMoV121. In such circumstances, the steam side oxidation rate assumes to be increasing also consider. Increasing the steam temperature leads to more rapid growth of oxide scale thickness, the heat transfer to steam, inside the tube is reduced. Hence, the wall temperature of the tube progressively increases with increasing service life. Such an increase in wall temperature not only leads to the more rapid accumulation of creep damage, it also result in higher fireside and steam side corrosion rates which increase thinning of the boiler tube and wall temperature and likely to progress ever more rapidly under a self accelerating process. Steam oxidation rates on 9Cr steels limits practical application to 600$^0$C.

**2.2 Materials use at 620$^0$C/325bar**

For steam condition of 325bar at 620$^0$C the metal temperature in the final superheater will be around 660$^0$C. Boiler tubes operating under these conditions will need 105 hours creep rupture strength of about 100MPa and a fireside co0rrosion rate leading to a maximum metals loss of 2mm in 100,000 hours. Both P91 and P92 are unlikely to possess sufficient fireside corrosion resistance in this application. However, it is hoped that these new higher creep strength, feritic steel will limit the cost impact by their selective use in cooler parts of the circuit. Austenitic material such as X8CrNiMoNb1616, X8CrNiMoVNb1613 and X3 CrNiMoNb1713 exhibit similar creep properties to the currently employed 12% CR steel such as X20CrMoV121, at a metal temperature 70 to 80 C higher. Increasing the chromium content of these steels confers a great resistance to fireside corrosion.

Whilst fine grained 347 HFG and super 304 steel both have the required creep rupture strength for operation up to 650$^0$C, the inadequate corrosion resistance conferred by chromium contents of around 18% may limit their operating temperature to 615$^0$-620$^0$C the tubes will also need to be manufactured from a material shoeing minimal steam side oxidation at these temperatures. This will be necessary in order to limit overall oxide growth.

For both NF709 and HR3C, the creep rupture data relate to tests of relatively short duration (circa 30,000 hours) and hence some caution should be exercised regarding the quotes strength values for operation to 100,000 hours. The final choice of material should be made on the basis of specific data, preferably obtained from tests on panels installed in operating plant. Currently, only data from short-term laboratory test on material exposed to idealized environments are generally available, these being inadequate for proper evaluation of performance over times relevant to plants.

**2.3 Materials use at 650$^0$C/350bar**

For tubes with metal temperature approaching 700$^0$C, enhanced versions of austenitic steel such as NF709, AC66, HR3C and HR6W will be required to limit the bore oxide thickness.

**3. Future R & D Requirement**

The future R & D requirement for boiler material may be summarized as follows:

1. T23 and 7CrMoVTiB1010appear to be the most likely materials of choice for the water walls tubes in supercritical plant operating up to 625$^0$C and 325 bar, but stronger material will be required for higher steam condition. The material at the most advanced stage or development at present T23 and 7CrMoVTiB1010 appear to be the most likely materials of choice for the water walls tubes in supercritical plant are P92, P122, and E911, but all three currently require post-weld heat treatment during fabrication.
2. Current materials are available for the manufacture of steam separating vessels for steam condition of up to 625$^0$C and 325bars. Where limitation of wall thickness criteria apply, stresses in the wall of these component may be reduced to acceptable levels by increasing the number of separator and reducing their duty. Stronger materials will be required for operation above 625$^0$C and 325 bars, with T91/P91 being a strongly favoured material.
3. Austenitic stainless steel which posses adequate creep rupture strength and fireside and steam side corrosion resistance are available for use in the final super heater tubes of advanced PF-fined plant operating with steam parameter up to 290bar/580$^0$C, provide the inherent flue gas corrosivity (CI content) is low. However, it is unlikely that the fireside corrosion resistance of these steel will be sufficient to operate much above 620$^0$C.
4. More highly alloyed steels are under development which may allow operation at steam temperature of up to 630$^0$C. However, more work is required to extend the creep rupture data for these steels out to longer times and longer term fireside corrosion data, collection under more realistic conditions, will be required before these materials can be used with any degree of confidence.
5. The higher creep strength of the austenitic steels and the somewhat lower metal temperature expected in header and the pipe work mean that less expensive grades, such as X3CrNiMoN1713, with lower chromium contents, can be considered then for tubing. A new heat resisting steel (0.1C-18Cr-10Ni-3Cu-Ti-Nb) named TEMPALOYAA-1 which has creep rupture 600-700, is under research at jarmany for ultra supercritical boiler material.
6. Some new clad material like HR11N, alloy 825, 304L, super alloy 625, carbonsteel SA210, also under research with respect to various properties of material, used for ultra supercritical boiler components in various countries like U.S.A, Japan & Germany etc.

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