Contemporary Engineering Sciences, Vol. 8, 2015, no. 29, 1371 - 1382
HIKARI Ltd, www.m-hikari.com
http://dx.doi.org/10.12988/ces.2015.58242

Martensitic and Austenitic Creep Resistant Steels for Application in Advanced Ultra-Supercritical Thermal Power Plants

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Abstract

The paper represents the results of investigation of martensitic and austenitic steels and their development in manufacturing of steam pipes and heating surface for advanced ultra-supercritical (A-USC) power plants with service steam temperature up to 680°C and pressure up to 32 MPa. There was shown that alloying by 3% Co of martensitic steels such as 9Cr-2W-Mo-VNb contributed to obtaining a high degree of dispersion of structure and improve creep resistance on 15-20% compared to steel type T/P92. Optimization of chemical composition and heat treatment parameters developed austenitic heat-resistant steel have provided a growth of long-term strength up to ~ 1.5 times (~ 96 N/mm2 at 680°C, 10^5h) in comparison with steels such as TP347. Steels were developed in manufacturing of parts of TPP equipment (headers, reheaters, steampipes etc.).

Keywords: martensitic steels, austenitic steels, ultra-supercritical parameters, A-USC

1 Introduction

High interest to the development of equipment for thermal power plants (TPP) with elevated steam parameters is linked to the economy of fuel, decrease of greenhouse gases (CO_2, NO_x, SO_x) emission and improvement of general efficiency [1, 2]. Currently there are considering several projects of thermal power plants with A-USC parameters for operating at temperatures above 700°C [3-6]. In comparison with TTP for 600°C /610°C such A-USC parameters could provide the reduction of emission by 25-30% and increase the efficiency of TPP by 5-8%.
It is necessary to note that the problem of increasing of service parameters advanced thermal power plants are linked with necessity of new expensive materials (e.g. Ni based superalloys) and solution of technical and technological problems of energy equipment manufacturing.
The bottleneck of the problem of development A-USC TPP is provision with materials and technologies which able to ensure safe operation of power equipment at elevated temperature for a life utility.
Among the currently available structural materials required level of creep resistance at temperatures ranging from 700°C to 750°C may be provided by using Ni based superalloys [7-9]. High relative material cost of nickel alloys (Fig.1) and the challenges that will be faced in the production of power equipment require the development of key technologies for which there are several problems [1]:

- Technology of production of large ingot out of Ni-based superalloys;
- Technology of manufacturing and heat-treatment of semi-finished products out of Ni-based alloys (forgings, pipes with large diameter and wall thickness etc.);

- Development of consumable materials, welding technology and heat-treatment parameters of similar and dissimilar weldments out of Ni-based super alloys.
- Accumulation of referential database of long-term tests results for new materials that would be ensure proper evaluation of reliability of energy equipment and life-time assessment.

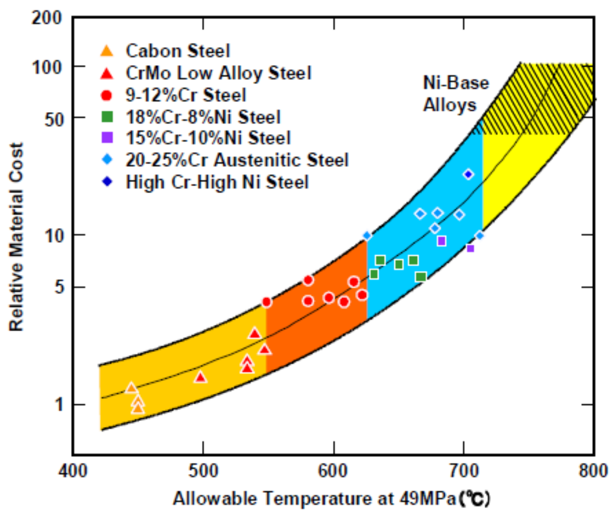

Fig.1 - Comparison of relative material cost with allowable temperature at 49MPa [1]

The presence of outstanding technical and technological issues with structure materials for elevating temperatures (above 700ºC) makes difficult economic assessment of return on investment for A-USC TTP construction. For that reason one of the alternatives seems to be a development of TTP for temperatures 650ºC - 680ºC based on advanced structure materials (i.e. martensitic and austenitic creep-resistant steels).
In this paper shows the results of investigation and manufacturing development of martensitic and austenitic steels for equipment of fossil power plants with maximum operating temperature up to 650ºC - 680ºC (headers, superheaters. steampipes, T-bends etc.).

2 Martensitic steels

Martensitic steels with 9-12%Cr are the most promising materials for the elements of the steam pipes with operating temperature above 620°C due the high creep resistance, toughness, ductility and fabricability. In addition to the above it’s necessary to solve the problem of significant improvement of creep resistance for these steels.

A lot of attention was given to investigation of these materials in the Russian Federation and the world from 1980s. In a result was developed such steels like X10CrMoVNb9-1 (T/P91), P92, E911, 10Ch9MFB, 10Ch9V2MFB for operating at temperatures up to 620ºC.
The high level of creep resistance of these steels ensured by chemical composition and martensitic structure and secondary phases ($M_{23}C_6$ and MX) that had been formed in the result of heat-treatment (quenching and tempering) [10].
In the course of creep tests and service operation, the chromium martensitic steels start to reveal that coagulation of large particles of the secondary phases (carbides $M_{23}C_6$ and Laves phases) along the grain boundaries would lead to degradation of the dislocation density, development of dynamic polygonization and transformation of the martensitic structure into a subgrain structural arrangement that, in turn, substantially reduces the creep resistance [11]. Achieving the maximum creep resistance at temperatures up to 650ºC requires having the formation of the coagulation-resistant secondary phases in the martensitic structure [10, 12].
One of the methods for improving the creep resistance is the method described in [12] and [13], i.e. feeding cobalt into the steel, limiting the precipitation of Laves phases and reducing the carbon content to the level, at which MX carbonitrides/nitrides (less prone to coagulation than carbides of the $M_{23}C_6$ type) make the main contribution to the precipitation strengthening.
Investigation of possibility of increasing of maximum allowable temperature of 9Cr martensitic steels was studied on a steel of base composition 10Ch9V2MFBR (Russian analog of steel P92).
As a result of complex researches aimed at the development of new materials was developed the family of steels such as 9Cr-3Co-2W-VNb with different carbon content - from 0.01% to 0.1%. Table 1 shows the chemical composition of the materials investigated.
Investigation of influence of alloying elements on phase composition of 9Cr-3Co-2W-Mo-V-Nb steel at operating temperatures was provided by thermodynamic calculation in Thermo-Calc software (DTB TCFE6.0).

Table 1. Chemical composition of steels

Heat №	**C**	**Si**	**Mn**	**Cr**	**Ni**	**Co**	**Mo**	**W**	**V**	**Nb**	**B (calc)**	**N**	**Al**	**S**	**P**
269	0,1	0,09	0,23	9,36	0,03	2,93	0,45	1,85	0,2	0,05	0,005	0,048	0,02	0,006	0,01
273	0,014	0,06	0,23	8,99	0,05	2,98	0,47	2,1	0,25	0,07	0,01	0,063	0,02	0,006	0,012

The thermodynamic modeling showed the practicability of alloying by cobalt in the amount of 3% and necessity of limitation of total amount of tungsten and molybdenum according equation W+2Mo ≤ 3.6%. Such equation between these alloying elements provides decreasing of the coagulation rate of $M_{23}C_6$ carbide for ~1.5 times (Fig. 2) in comparison with steels such as P92 and limiting the Laves phase content, the precipitation of which leads to the tungsten and molybdenum depletion of the solid matrix solution and also weakens the effect of solid solution hardening.

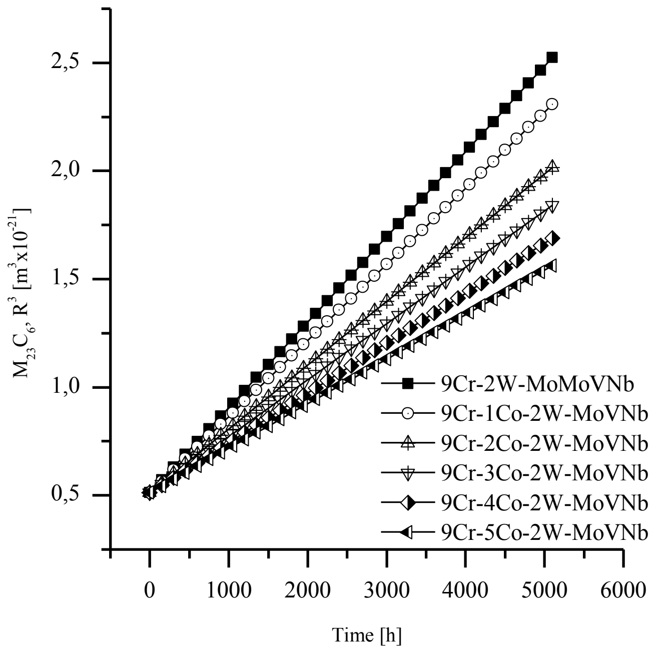

Fig.2 Time dependent coarsening of $M_{23}C_6$ at 650°C
in 9Cr-*x*Co-2W-MoVNb (*x* = 0 – 5 wt.%)

The structure of the steels (heats 269 and 273) after heat treatment is tempered martensite and have showed on a fig.3. The average size of the prior austenite grain (PAGB) in these steels makes up 10 μm at a carbon content of 0.1% and 16 μm with a carbon content of 0.014%, and this is smaller than the PAGB size (20 μm [10]) in the steel of the P92 type.

In the process of tempering, the 0.1C-9Cr-3Co-2W-Mo-V-Nb steel shows that the precipitation of the secondary (predominantly $M_{23}C_6$) phases with an average size, ranging from 50 to 100 nm has been taking place along the boundaries of blocks and prior austenite grains. Inside the laths, the homogeneously distributed carbonitrides of the MX type, ranging in size from 5 to 40 nm, can be observed. The reduction in the carbon content in the steel from 0.1% to 0.014% results in substantial reduction of the volume fraction of carbides $M_{23}C_6$ while their sizes are maintained at the same level.

As can be seen from the above data, alloying of steel by 3% of cobalt contributed to disintegration of the structure, scaling down the sizes of PAGB and having the dispersed secondary phases. Reducing carbon in the 9Cr-3Co-2W-MoVNb steel from 0.1% to 0.014% resulted in decreasing the fraction of the $M_{23}C_6$ type carbides and partial replacement of hardening with $M_{23}C_6$ carbides by the carbonitride hardening with MX particles.

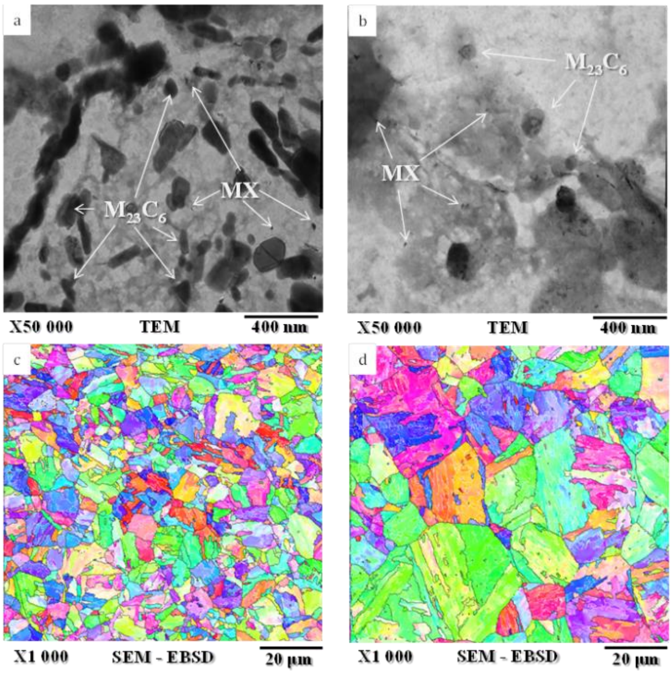

Fig.3 Microstructure and orientation maps of 9Cr-3Co-2W-MoVNb steel with 0,1wt.% (a, c) and 0.014wt.%(b,d) of carbon

The difference in the chemical composition and microstructure of the heats #269 and #273 has not produced any substantial changes in the mechanical properties of the metal (Table 2). Hardness, flow limit and strength limit after thermal treatment of the both steels are essentially identical. At the same time, reduction of the carbon content and feeding of cobalt have a noticeable effect on the high-temperature strength of the steel at 650°C.

Comparison of the long-term strength test results (Fig. 4) for the heats #269 and #273 with P92 steel shows that alloying by 3% of cobalt in the steel 9Cr-2W-MoVNb improve the long-term strength limit over 10^5 hours at 650°C for about 30% and that for the steel with a carbon content of 0.014% by 40% in comparison with the T/P92 steel, but in such case, the toughness value decreases significantly.

Table 2. Mechanical properties of 9Cr-3Co-2WMoVNb steels

	Temperature	σ_b, N/mm^2	$\sigma_{0,2}$, N/mm^2	δ_5, %	Ψ, %	Hv
Heat #269	20°C	701 713	530 550	19,8 20,3	70,0 73,0	251
	650°C	282 310	259 292	22,0 23,5	88,0 89,0	-
Heat #273	20°C	666 671	564 567	17,5 18,0	70,0 70,0	253
	650°C	327 363	307 355	14,0 15,0	82,0 83,0	-

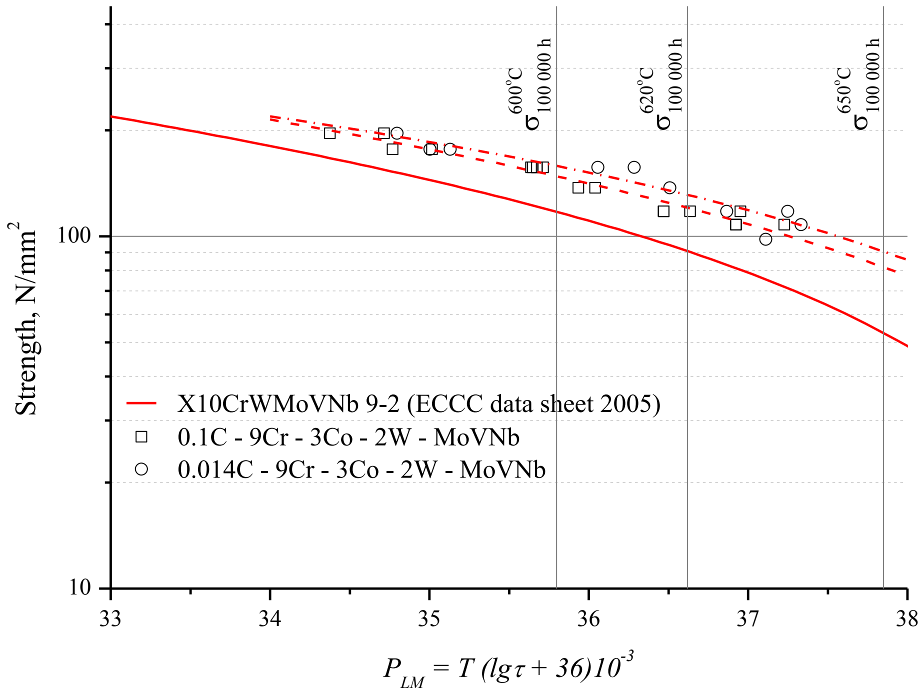

Fig.4 Creep data of tempered P92 steel and 9Cr-3Co-2W-MoVNb steel

3 Austenitic steels

Russia has experience in development, construction and service of equipment with ultra-supercritical steam parameters:

- Pilot boiler on testing site of JSC VTI with steam operating temperature up to 650°C and pressure up to 30.0 MPa worked more than 200 000 hours. Currently it has operable state and could be used for researches.

- Power-generating unit SKR-100 (Kashirskaya TTP) with boiler steam capacity 720 t/h and steam parameters on 650^{o}C and 30 MPa was operated from 1969 yr. (~100 000 hours).

Another aim of this work was development of creep-resistant austenitic steel for the super-heaters with steam operating temperature up to 680^{o}C, pressure up to 32 MPa for a life-time up to 200,000 hours.
For the purpose of achievement of desirable creep rupture strength level at 680^{o}C the development of austenitic creep resistant steel was based on a "16Cr-16Ni" system (e.g. SANDVIK 12R72HV, EP-184). As a result of optimization of content of alloying elements and heat treatment parameters provides a rise of efficiency of matrix strengthening through the solid solution hardening and formation of secondary phase ($M_{23}C_6$ carbides, TiCN carbonitrides), steel 15Cr-16Ni-2Mo-Ti-B was developed (table 3).

Table 2. Chemical composition of austenitic 15Cr-16Ni-2Mo-Ti-B steel

C	Si	Mn	S	P	Cr	Ni	Ti	Mo	B
0,11	0,4	1,7	0,009	0,012	15,70	16,0	0,47	2,3	0,008

The highest degree of doping γ-solid solution is achieved with increasing of temperature of austenitization, which lead to the grain growth and the development of recrystallization and reducing the stress rupture ductility. Studying of dissolving process the excess phases at temperature range from 1050°C to 1250°C have shown the practicability of choosing temperature 1200°C for austenitization because it's provides an optimal solution hardening, grain size and content of TiCN carbonitrides.
The steel microstructure after austenitization in the initial state is the austenite structure, with grain size about ~44 mm (Grade 6 according GOST-5639) with primary inclusions of titanium carbonitrides and low content of secondary phases at grain boundaries and inside the grains (fig.5).

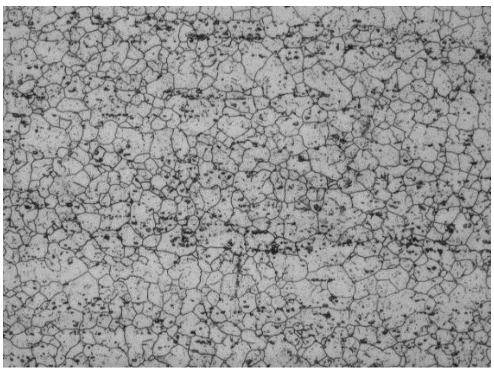

Fig.5 – Microstructure of 15Cr-16Ni-2Mo-Ti-B steel (x200)

The resulting steel structure provides high level of short-term and creep rupture strength. The value of tensile strength of 660-675 N/mm^2, yield stress - 290-302 N/mm^2, the contraction ratio and elongation - 38 - 43% and 64 - 72%, respectively.

Strength factor at the room temperature was defined according to the standards for structural calculations for austenitic steels: for tensile strength – 4.5 (rated value 3.0), for yield strength – 2.0 (rated value 1.5).
The values of short-term strength at the operating temperatures keep the high level, i.e. tensile strength is about 330-435 N/mm^2, yield strength is about 152-187 N/mm^2. Creep rupture strength defined for 10^5 hours at 680°C is 96 N/mm^2.

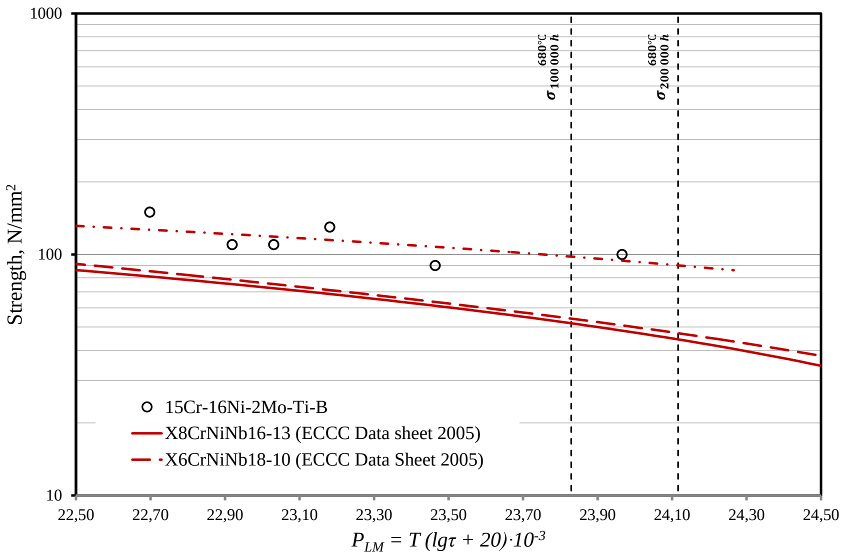

Fig.6 - Creep data of 15Cr-16Ni-2Mo-Ti-B, X8CrNiNb16-13 and X6CrNiNb18-10 steels

4 Materials development

Austenitic and martensitic steels was developed in manufacturing of parts of TPP equipment (headers, reheaters, steampipes etc.) on the main metallurgical and engineering factories, i.e. Urals Stampings Plant (Mechel Group), Metallurgical Plant “Electrostal”, Chelyabink pipe-rolling plant, Pervouralsk new pipe plant, Voljskiy pipe plant, The Taganrog Boiler-Making Works “Krasny Kotelshchik”, The Belgorod Boiler-Making Works. Was manufactured (fig. 7):
- ingots (D > 540 mm);
- round bar (D > 150 mm);
- forgings (D > 250 mm);
- tubes and pipes for headers, steam pipes and reheaters (32 mm < OD < 325 mm);
- bends;
- similar and dissimilar weldments of pipes.

In industrial production steels have shown good fabricability, current technologies provide required level of products quality.

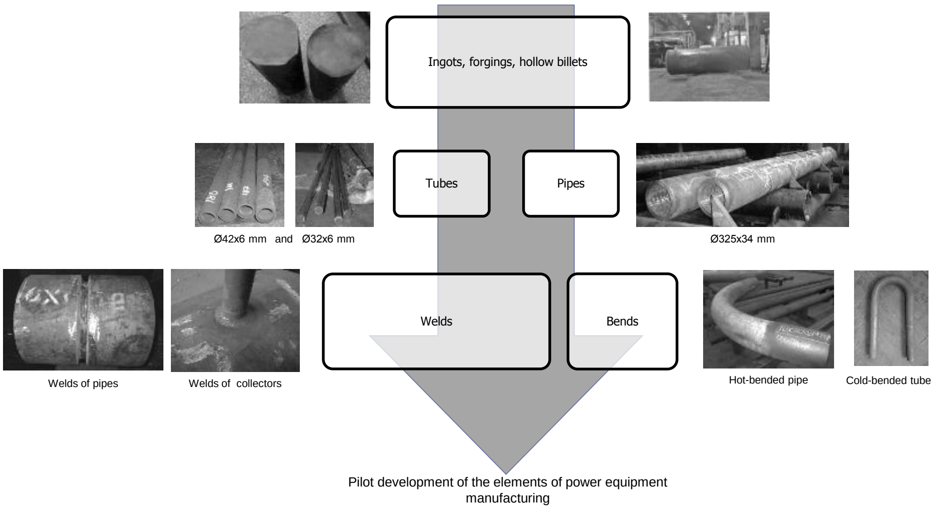

Fig.7 - Stages of development

5. Conclusion

One of the scenario of improving advanced ultra supercritical thermal power plants is developing TTP for temperatures 650ºC - 680ºC using the advanced austenitic and martensitic steels. For that purpose new kind of steels 0.1C-9Cr-3Co-2W-VNb and 15Cr-16Ni-2Mo-Ti-B were developed in the Russian Federation. Steels have shown a high level of service properties and fabricability in manufacturing of parts of TPP equipment (headers, reheaters, steampipes etc.).

Acknowledgements. This study was conducted by JSC RPA "CNIITMASH" and National Research University "Moscow Power Engineering Institute" and has been financially supported by the Russian Federation through the Ministry of Education and Science of the Russian Federation under Subsidy Agreement №14.574.21.0098 of August 22nd 2014, as a part of the Federal Targeted Program for R&D in Priority Fields for the Development of Russia's S&T Complex for 2014-2020. Applied Scientific Research Unique Identifier: RFMEFI57414X0007.

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Received: September 7, 2015; Published: October 21, 2015