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Creep-resisting structural steels for the power industry – past and present

Abstract: The article provides information about the condition of domestic and global power industries in the context of the thermal efficiency of existing power systems. The work also presents the tendencies in the development of power systems operating at supercritical steam parameters. The article shows the basic requirements for advanced structural materials intended for use in power industry machinery and also presents diagrams showing the development of successive creep-resisting steel generations with the ferritic base and of austenitic steels. The article provides approximate chemical compositions of selected steels from individual groups differing in chromium content. Attention is also given to the dependence of welding process technological parameters for joining steels designed for higher temperatures on the chemical composition of the steels and the thickness of the components being welded. The conclusion contains a statement that the continuous introduction of new steel grades on the market is accompanied by the continuous use of steels belonging to older generation grades such as 13CrMo4-5 and 10CrMo9-10 ones.

Keywords: power industry, creep-resisting steel, supercritical parameters;

Introduction

This study is the result of work based on accessing available scientific and popular-science publications, mainly from the early years of the 21st century, related to tests of structural steels for the power industry and the developmental progression of these steels.

Since electric energy started being generated on an industrial scale at the end of 19th century, mainly using coal, the principal parameter defining the modernity of a unit or a given technology has been its thermal efficiency.

According to publicised data [3] the net efficiency of the best Polish power plants amounts on the average to 33%, in the world to 36%, and in newly built power units even to 42-46%. The thermal efficiency of power plants can be improved by using the supercritical parameters of steam, i.e. a temperature of over 540°C and a pressure of 18 MPa. It is estimated that increasing steam temperature from 540°C to 650°C and pressure from 18 MPa to 30 MPa enables a 10% increase in the efficiency of power generating equipment [4].

The potential of conventional power engineering is made by power plants and combined heat and power plants using mainly brown and carbon coal. As regards the generation of electric energy, power plants can be divided into steam power plants and those equipped

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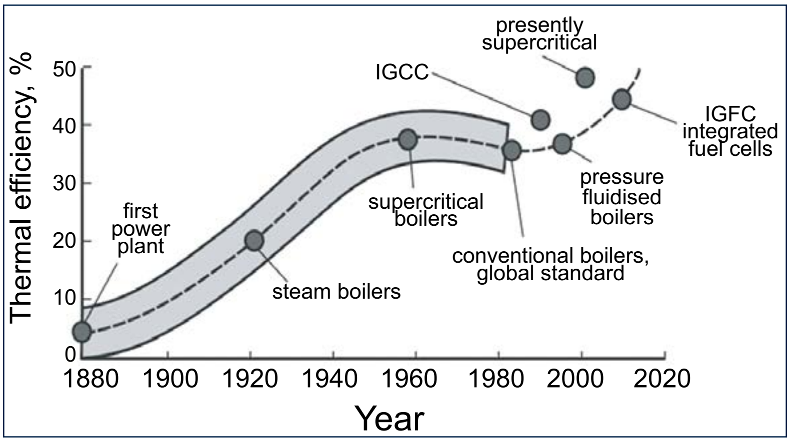

Fig. 1. Development of electric energy generation technologies based on burning coal [1-3]

in the power industry would be impossible without the development of structural materials, mainly steels, intended for operation at a heightened temperature.

Division of structural steels intended for operation at increased temperature

Creep-resisting steels include a large group of structural steel grades differing in their chemical composition with a microstructure obtained as a result of heat treatment and intended use for a specific range of power systems.

The development of thermal power engineering towards the use of higher operating parameters (temperature and pressure), and thus obtaining a greater efficiency, depends on the availability of appropriate structural materials.

with gas turbines. The continual popularity and continuous growth of investments connected with the development of steam power plants is reflected by the results of surveys and investigations monitoring the development of such structures in the world (Fig. 2). It is possible to observe an interest in power units in operation with supercritical parameters and projects and investments related to units with a power of 400-1000 MW for a steam pressure of 25-30 MPa and an operating temperature in the range 580-610°C, carried out mainly in the USA and Japan. Currently implemented research projects involve even higher operating parameters in which temperature is restricted within the range 620-650°C (though sometimes reaching 700°C) and a pressure exceeding 30 MPa [3].

An example of the development of carbon coal burning power units in Germany is presented in Figure 3.

The development and use of supercritical parameters has enabled the construction of power units having net thermal efficiency reaching 48% which simultaneously reduce the emission of noxious pollutants to the atmosphere and cut down electric energy generation costs.

The aforesaid development of technologies concerned with the manufacturing and operating of equipment

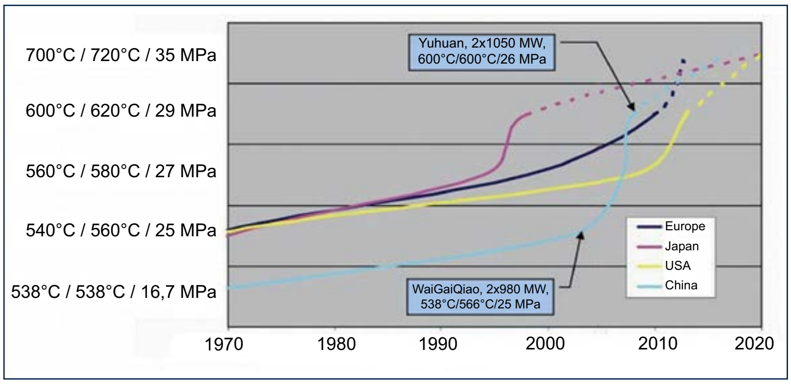

Fig. 2. Forecast development of steam power plants in Europe, Japan, USA and China until 2020 [5]

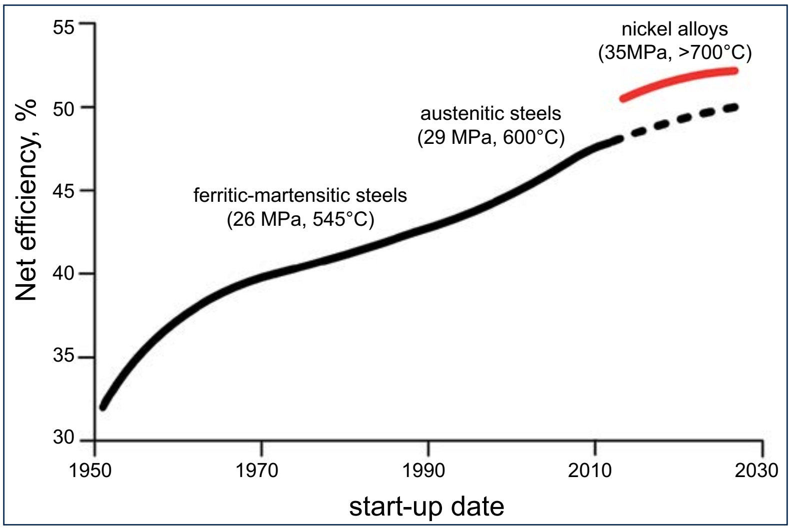

Fig. 3. Development of carbon coal burning power units in Germany [6-8]

In the boiler part of a power unit the most important elements include tight walls made of thin-walled pipes, steam superheaters and re-superheaters, as well as thick-walled live steam pipelines and chambers. Requirements for each of the enumerated elements include thermal formability, weldability and heat treatment, as well as [9, 10] the following:

- proper mechanical properties, aimed to ensure long-lasting operation at a high temperature and under pressure (creep strength) taking into account the cyclicity of loads (resistance to low-cycle thermal fatigue),
- proper oxidation resistance, so that the growth of an oxide film inside the pipes does not cause an excessive increase in the temperature of the pipe walls,
- proper corrosion resistance in order to ensure the smallest possible material losses from the furnace side.

Due to the microstructure and operating temperature creep-resisting steels can be divided into the following:

a) ferritic steels (ferritic-pearlitic, ferritic-bainitic, bainitic and martensitic),

b) austenitic steels.

The highest operating temperature of CMn-type unalloyed steels is assumed to be within the range of 400-450°C. For molybdenum steels and 0.5Mo, 1Cr-0.5Mo, 2.25Cr-1Mo and Cr-Mo-V type chromium-molybdenum steels, depending on the grade, operating temperature is contained within the range from 540°C to 565°C. Steels having a martensitic microstructure with a carbon content of 0.07-0.22%, a chromium content of 8-12% and containing molybdenum, tungsten, nickel, niobium, vanadium and boron additions can be used up to a temperature of 600°C, whereas steels with a cobalt addition are expected to be used up to a temperature of 620°C [11]. Austenitic steels can be used successfully up to a temperature of 700°C.

Corrosion and oxidation resistance at a heightened temperature depends mainly on

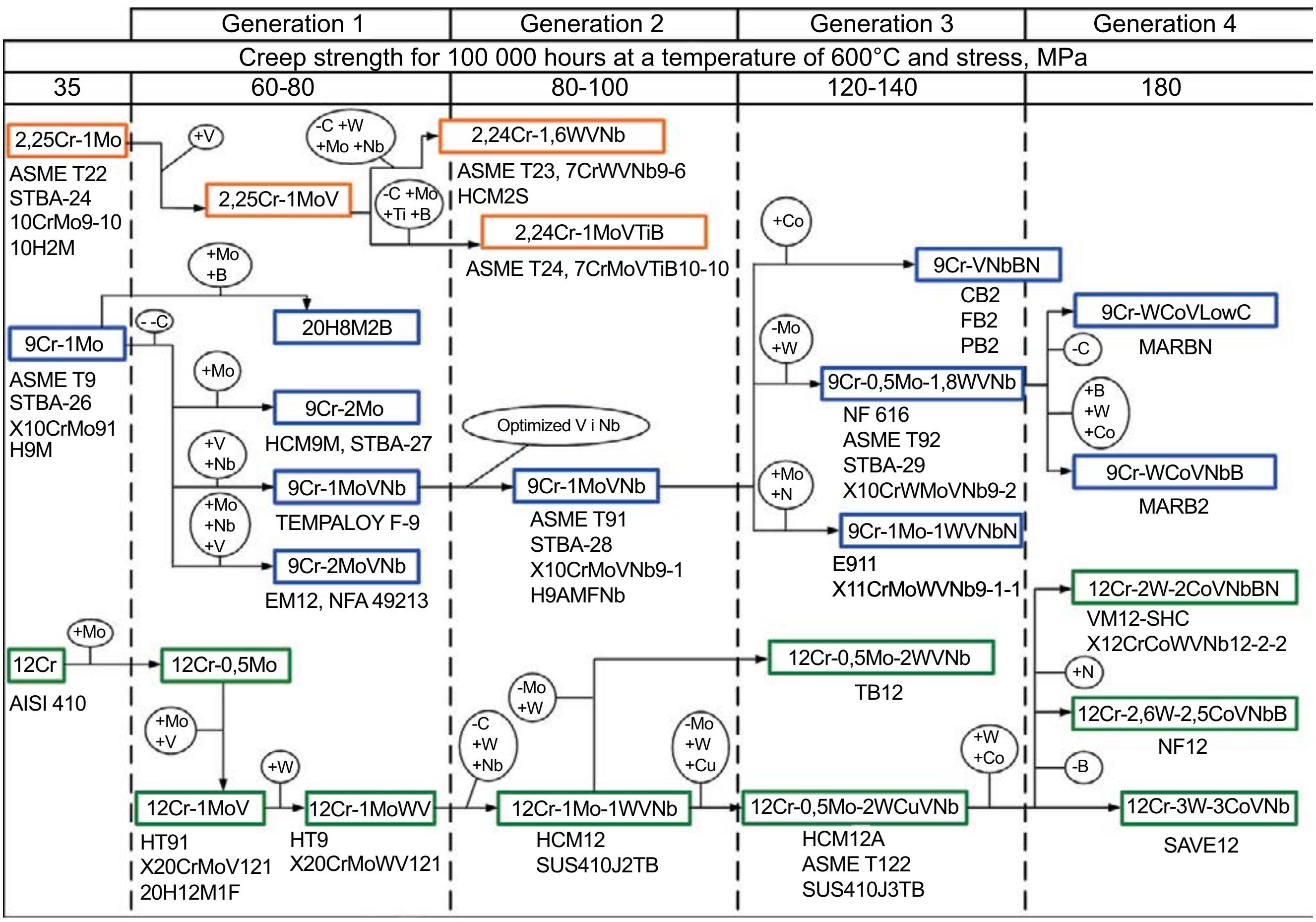

Fig. 4. Scheme of development of ferritic steels intended for operation at heightened temperature [12, 13]

Table 1. Chemical composition of ferritic steels intended for operation at heightened temperatures [11, 14-22]

Steel	Element content,%																
	C	Mn	Si	P	S	Cr	Ni	Mo	V	Ti	Nb	W	Co	Cu	B	Al	N
Steels of content from approximately 0.5 to 2.25% Cr																	
T22 (10CrMo9-10)	0,05 - 0,15	0,30 - 0,60	max. 0,50	max. 0,025	max. 0,025	1,90 - 2,60	-	0,87 - 1,13	-	-	-	-	-	0,25	-	max. 0,040	≤ 0,012
16Mo3	0.12 - 0.20	0.40 - 0.90	0.17 - 0.37	max. 0.035	max. 0.035	max. 0.30	max. 0.30	0.25 - 0.35	max. 0.02	max. 0.05	max. 0.01	max. 0.10	max. 0.10	0.30	-	max. 0.10	-
13CrMo4-5	0.08 - 0.18	0.40 - 1.00	0.10 - 0.35	max. 0.025	max. 0.010	0.70 - 1.15	max. 0.40	0.40 - 0.60	max. 0.10	max. 0.05	-	max 0.10	-	0.30	-	max. 0.10	-
14MoV63	0.10 - 0.18	0.40 - 0.70	0.15 - 0.35	max. 0.040	max. 0.040	0.30 - 0.60	max. 0.30	0.50 - 0.65	0.22 - 0.35	-	-	-	-	max. 0.25	-	max. 0.020	-
T/P23	0.04 - 0.10	0.10 - 0.60	max. 0.50	max. 0.030	max. 0.010	1.90 - 2.60	max. 0.40	0.05 - 0.30	0.20 - 0.30	0.005 - 0.060	0.02- 0.08	1.45 - 1.75	max. 0.10	max. 0.30	0.001 - 0.006	max. 0.03	max. 0.03
T/P24	0.05 - 0.10	0.30 - 0.70	0.15 - 0.45	max. 0.020	max. 0.010	2.20 - 2.60	-	0.90 - 1.10	0.20 - 0.30	0.05 - 0.10	-	-	-	-	0.002 - 0.007	0.02	0.010
Steels of content of approximately 9% Cr																	
H9M	max. 0.12	0.30 - 0.60	0.25 - 1.00	max. 0.035	max. 0.030	8.00 - 10.00	-	0.90 - 1.20	-	-	-	-	-	max. 0.30	-	-	-
HCM9M	max. 0.08	0.30 - 0.70	max. 0.05	max. 0.03	max. 0.03	8.00 - 10.00	-	1.80 - 2.20	-	-	-	-	-	-	-	-	-
T/P91	0.08 - 0.12	0.30 - 0.60	0.20 - 0.50	max. 0.020	max. 0.010	8.00 - 9.50	0.40	0.85 - 1.05	0.18 - 0.25	-	0.06 - 0.10	-	-	-	-	0.04	0.03 - 0.07
E911	0.09 - 0.13	0.30 - 0.60	0.10 - 0.50	max. 0.020	max. 0.010	8.50 - 9.50	0.10 - 0.40	0.90 - 1.10	0.18 - 0.25	-	0.060 - 0.100	0.90 - 1.10	-	-	max. 0.006	-	0.050 - 0.090
T/P92 (NF616)	0.07 - 0.13	0.30 - 0.60	max. 0.50	max. 0.020	max. 0.010	8.50 - 9.50	max. 0.40	0.30 - 0.60	0.15 - 0.25	-	0.040 - 0.090	1.50 - 2.00	-	-	0.001 - 0.006	0.04	0.030 - 0.070
PB2	0.12 - 0.14	0.30 - 0.40	0.05 - 0.10	max. 0.009	max. 0.003	9.00 - 9.50	0.10 - 0.20	1.40 - 1.60	0.18 - 0.22	0.003	0.04 - 0.065	-	1.20 - 1.40	0.10	0.006 - 0.010	0.005 - 0.010	0.015 - 0.030
MARBN	0.076 - 0.081	0.49 - 0.51	0.30 - 0.31	max. 0.020	max. 0.010	8.88 - 9.08	-	-	0.19 - 0.20	-	0.049 - 0.055	2.85 - 3.07	3.00 - 3.03	-	0.0132 - 0.0150	-	0.0015 - 0.0650
Steels of content of approximately 12% Cr																	
X20Cr-MoV121	0.17 - 0.23	max. 1.00	max. 0.50	max. 0.035	max. 0.035	10.00 - 12.50	0.30 - 0.80	0.80 - 1.20	0.25 - 0.35	-	-	-	-	-	-	-	-
HCM12	max. 0.14	max. 0.70	max. 0.50	max. 0.030	max. 0.030	11.00 - 13.00	-	0.80 - 1.20	0.20 - 0.30	-	max. 0.20	0.80 - 1.20	-	-	-	-	-
HCM12A	0.07 - 0.14	max. 0.70	max. 0.50	max. 0.015	max. 0.001	10.00 - 12.50	max. 0.50	0.25 - 0.60	0.15 - 0.30	-	0.04 - 0.10	1.50 - 2.50	-	0.30 - 1.70	max. 0.005	max. 0.040	0.040 - 0.100
TB12	0.10 - 0.15	max. 0.50	max. 0.04	max. 0.020	max. 0.010	11.00 - 13.00	0.70 - 1.00	0.40 - 0.60	0.15 - 0.25	-	0.04 - 0.09	1.60 - 1.90	-	-	-	-	0.04 - 0.09
NF12	max. 0.08	max. 0.50	max. 0.05	max. 0.020	max. 0.010	11.50	max. 0.50	0.15	0.20	-	0.07	2.6	2.5	-	0.004	-	0.05
VM12-SHC	0.10 - 0.14	0.15 - 0.45	0.40 - 0.60	max. 0.020	max. 0.010	11.0 - 12.0	0.10 - 0.40	0.20 - 0.40	0.20 - 0.30	0.005 - 0.018	0.030 - 0.080	1.30 - 1.70	1.40 - 1.80	0.25	0.003 - 0.006	0.02	0.030 - 0.070

the chromium content of a steel. In turn, appropriately high creep strength of ferritic steels is obtained due to the microstructure of tempered martensite and additions of strongly carbide-forming elements such as molybdenum, niobium, vanadium and tungsten [4]. A scheme of the development of ferritic steels is presented in Figure 4, and the chemical composition of the most popular steels of this group is presented in Table 1.

An extremely important problem for welding practice is the deteriorating weldability of structural steels along with an increase in the content of alloying elements manifested not only by the necessity of taking safety precautions during welding, such as pre-heating, monitoring interpass temperature during welding and the use of post-weld heat treatment (PWHT) of joints, but first of all by constricting the ranges of welding process technological parameters, as presented in Figure 5. In turn, the development of austenitic steels is presented in Figure 6, and the chemical composition of new generation steels used in the production of power boilers is presented in Table 2.

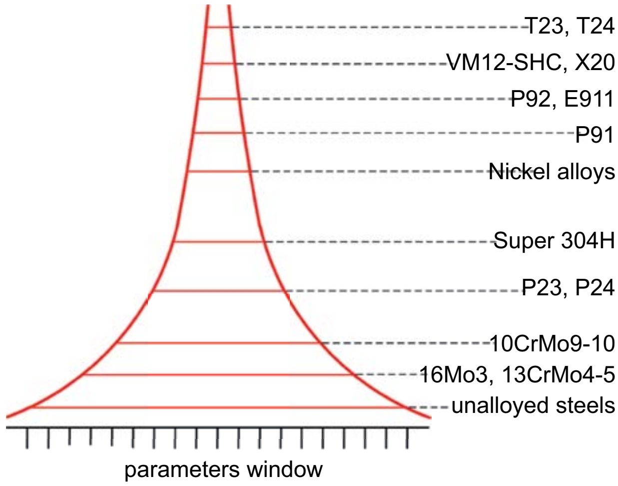

Fig. 5. Dependence of range of steel welding technological parameters for operation at heightened temperatures on chemical composition and assortment of steel (wall thickness) [23]

The National Institute for Materials Science in Japan has developed a prototypical steel named MARBN (MAR - martensite, B - boron, N - nitrogen) [25] as an alternative to the P92 steel.

Table 2. Chemical composition of austenitic steels used in power industry [10, 24]

Steel group	Steel designation according to ASME	JIS	Element content in% C	Mn	Si	Cr	Ni	Mo	V	Ti	Nb	W	B	Other
18Cr-8Ni	TP304H	SUS304HTB	0.08	1.6	0.4	18.0	8.0	-	-	-	-	-	-	-
	Super 304H	SUS304J1HTB	0.10	0.8	0.2	18.0	9.0	-	-	-	0.40	-	-	3.00 Cu 0.10 N
	TP321H	321FHTB	0.08	1.6	0.6	18.0	10.0	-	-	-	-	-	-	-
	TEMPALOY A-1	SUS321J1HTB	0.12	1.6	0.6	18.0	10.0	-	-	0.08	0.10	-	-	-
	TEMPALOY AA-1	SUS321J2HTB	0.12	1.6	0.6	18.0	10.0	-	-	0.10	0.20	-	0.002	3.00 Cu
	TP316H	SUS316HTB	0.08	1.6	0.6	18.0	12.0	2.5	-	-	-	-	-	-
	TP347H	TP347HTB	0.08	1.6	0.6	18.0	10.0	-	-	-	0.80	-	-	-
	TP347HFG	-	0.08	1.6	0.6	18.0	10.0	-	-	-	0.80	-	-	-
15Cr-15Ni	17-14CuMo	-	0.12	0.7	0.5	16.0	14.0	2.0	-	0.30	0.40	-	0.006	3.00 Cu
	Esshete 1250	-	0.12	6.0	0.5	15.0	10.0	1.0	0.2	0.06	1.00	-	-	-
20-25Cr	TP310	SUS310TB	0.08	1.6	0.6	25.0	20.0	-	-	-	-	-	-	-
	TP310NbN (HR3C)	310J1TB	0.06	1.2	0.4	25.0	20.0	-	-	-	0.45	-	-	0.20 N
	Alloy 800H	NCF800HTB	0.08	1.2	0.5	21.0	32.0	-	-	0.50	-	-	-	0.40 Al
	TEMPALOY A-3	SUS309J4HTB	0.05	1.5	0.4	22.0	15.0	-	-	-	0.70	-	0.002	0.15 N
	NF709	SUS310J2TB	0.15	1.0	0.5	20.0	25.0	1.5	-	0.10	0.20	-	-	-
	SAVE25	-	0.10	1.0	0.1	23.0	18.0	-	1.5	-	0.45	1.5	-	3.00 Cu 0.20 N
High content of Cr and Ni	CR30A	-	0.06	0.2	0.3	30.0	50.0	2.0	-	0.20	-	-	-	0.03 Zr
	HR6W	-	0.08	1.2	0.4	23.0	43.0	-	-	0.08	0.18	6.0	0.003	-

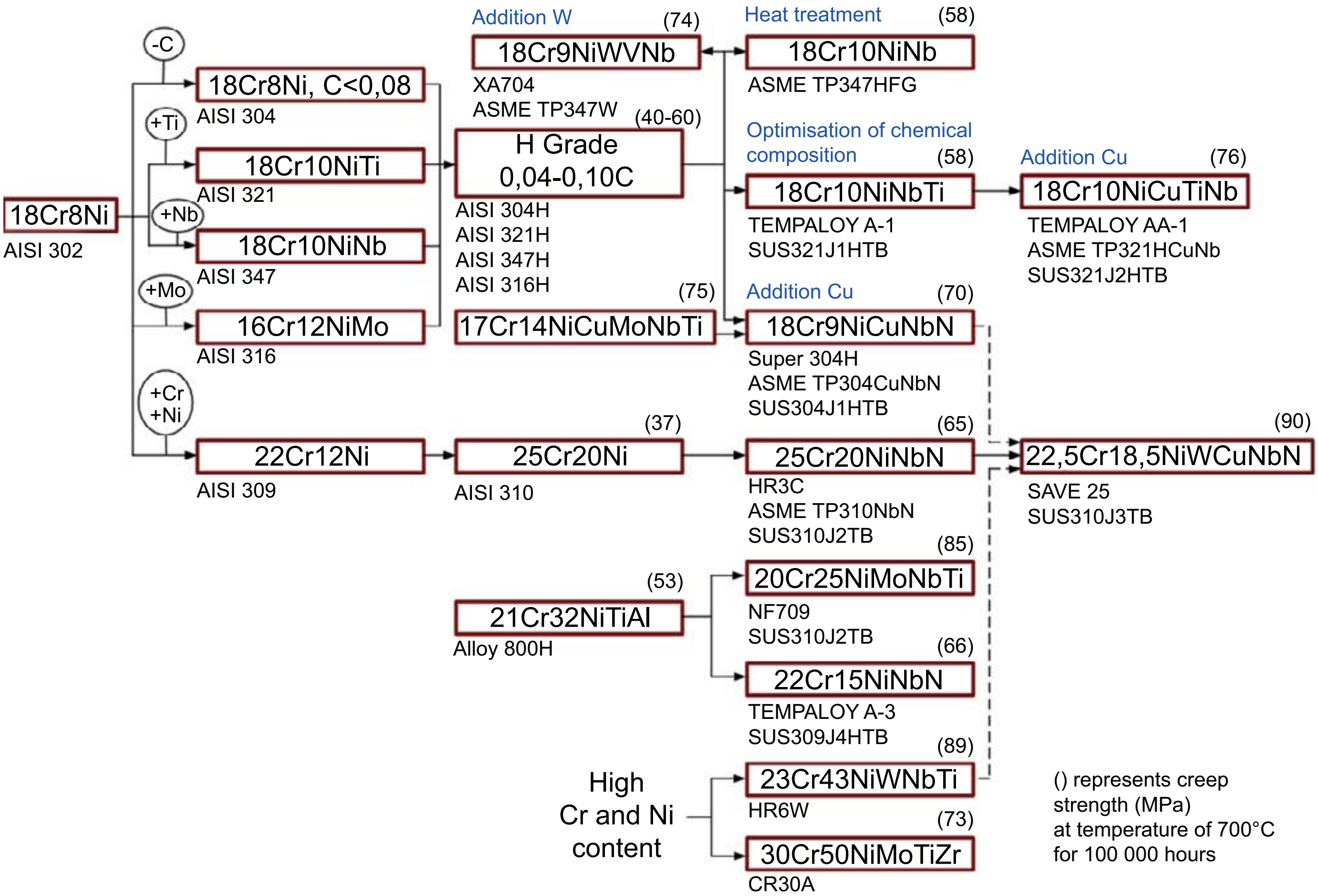

Fig. 6. Development of austenitic steels intended for devices in power engineering [12]

The MARBN steel is a martensitic steel and, similarly to the P92 steel, contains approximately 9% chromium. A novelty is the introduction of strictly controlled boron and nitrogen contents to its chemical composition in order to significantly improve the creep strength of the steel at an operating temperature of 650°C. As opposed to the P92 steel, the MARNB steel does not contain molybdenum, which is a completely new solution in the group of steels having a non-austenitic structure intended for use in power engineering. The approximate chemical composition of the MARBN steel is presented in Table 1.

Reference publications also contain information regarding the results of the tests of structural steels modified with nitrogen. An example is an unalloyed steel with an approximate chemical composition containing 0.1%C; 1.5%Mn; 0.015%Ti and 40-170 ppm N; Ce = 0.35, in which, owing to appropriate Ti/N proportions it was possible to obtain an unexpected effect. Following the welding of the steel, in the HAZ area of a joint it was possible to obtain a significantly visible restriction of the width of a coarse-grained zone (CGHAZ – coarse-grained HAZ), which in turn enabled an increase in the crack resistance of a welded joint [26]. An example of the case under discussion is presented in Figure 7.

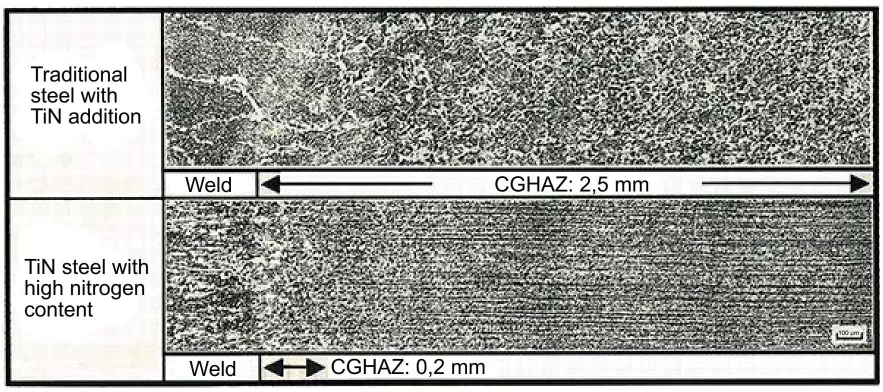

Fig. 7. Comparison of microstructure of HAZ in welded joint of traditional steel stabilised with titanium and nitrogen addition (top)and steel with high nitrogen content (bottom) [26]

Summary

Based upon data available in reference publications it is possible to conclude that the situation of structural steels for conventional power engineering is stable. The necessity of increasing the efficiency of power units, and thus the necessity of building high-power boilers of supercritical parameters, entails the development of steels operating in creep conditions. At present, an example of the progress in modern materials of this type is the X12CrCoWVNb12-2-2 martensitic steel with the addition of cobalt and tungsten known in Europe as the VM12-SHC steel or the new X13CrMoCoVNbNB9-2-1 steel designated with an interim symbol of PB2.

Among the analysed groups of structural materials for conventional power engineering structures steels having the greatest chances of use in the future are the following:

a) unalloyed steels having a ferritic-pearlitic structure: 13CrMo4-5 (equivalent of the 15HM steel) and 10CrMo9-10 (equivalent of the 10H2M steel);
b) alloyed steels having a bainitic structure: 7CrWVMoNb9-6 (T/P23) and 7CrMoVTiB10-10 (T/P24);
c) alloyed steels having a martensitic structure: X10CrMoVNb9-10 (T/P91), X10CrWMoVNb9-2 (T/P92), X12CrCoWVNb12-2-2 (VM12-SHC) and 12Cr3W3CoVNbTaNdN (SAVE12);
d) alloyed steels having an austenitic structure: 18Cr8NiWNbN (Super 304H), X7CrNiNb18-10 (347H) and 25Cr20Ni0.4Nb0.2N (HR3C).

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