STRUCTURAL STABILITY OF NEW CREEP-RESISTING STEEL GRADES WITH 9 AND 12% Cr CONTENTS APPLIED IN POWER GENERATION SECTOR IN INDUSTRIAL CONDITION

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ABSTRACT

The article presents RAFAKO S.A. experience within the field of selection of filler metals, welding processes, implementation of new steel grades as well as selected results of examinations of welded joint properties of new generation creep-resisting steel grades - including those with the addition of tungsten - for their weldability, strength and process properties. It also presents the results of strength examinations of steam superheater elements with 38 mm diameter and 4,4; 6,3 mm wall thickness, made of martensitic creep-resisting steel grades HCM12 and HCM12A (T122) containing 12% Cr as well as P92 steel grade containing 9% Cr, including the results of the assessment of welded joints structure, heat affected zone after relief annealing and structure stability after simulated operating conditions (ageing) and after c.a. 20 000 hours of operation in actual boiler operating conditions. Said examinations were carried out in RAFAKO S.A. within the framework of COST 522 program.

KEYWORDS

power generation, supercritical parameters, creep-resisting steel, weldability, properties of welded joints, microstructure stability,

INTRODUCTION

Within the period from 1995 to 2000 the average efficiency of local utilities amounted to c.a. 33% while the efficiency values of new power-generating units installed in Europe approached the range of 42-46%. In line with a decision to build a 440 MW power-generating unit in Pątnów Power Plant, the main guidelines of country's energy policy stipulate the construction of another 440 MW power-generating unit in Łagisza Power Plant and 840 MW power-generating unit in Bełchatów Power Plant, both operating with supercritical parameters of the medium, i.e. steam temperature reaching 580-620°C, steam pressure amounting to 26-30 Mpa and design unit efficiency of 43-46 %. These newly designed boilers shall also meet very stringent requirements concerning availability and environment protection resulting from the provisions of European Directive no. 80/2001/EU [1-3].

Such boiler design parameters require the application of new generation martensitic steel grades with 9 - 12% Cr contents and tungsten addition in manufacturing of outlet superheaters elements.

This clear tendency to increase power plant efficiency - and, in particular, the efficiency of powergenerating units with supercritical steam parameters - has resulted in last 10 years in development of a whole series of new creep-resisting steel grades, which are able to be used in outlet steam temperatures of c.a. $620 (650)^{\circ}$ C. In case of a typical "supercritical" unit, with steam temperature of c.a. 600° C and steam pressure of c.a. 270 bar - with steam reheat in secondary part up to 600° C applied creep-resisting steel grades have to assure the required creep resistance of individual boiler components in design temperatures, as follows: [4-6]:

- up to 500° C for elements of boiler membrane walls,
- up to $600 (620)^{0}$ C for large thickness boiler elements located outside the flue gas zone,
- up to 630 (650)⁰C for steam superheater elements located within the flue gas zone [6-10].

Considerable European contribution, which has helped to determine the directions of development and the scope of modifications of new martensitic steel grades consists in European COST 522 currently COST 536 - program "Power Generation into the 21st Century; Advanced Steam Power Plant" [12-21]. Already in the year 2000, Rafako S.A., in co-operation with Welding Institute and IMŻ Gliwice, commenced its participation in COST 522 program quickly becoming one of the major participants. The objective of RAFAKO S.A. participation in COST 522 program was to recognize current directions of development of creep-resisting steel grades combined with use of its large manufacturing and implementation capacities in applications of new materials, optimising of manufacturing processes such as welding, plastic forming as well as implementation of new techniques of examinations of power-generating equipment for both local and European Community markets[5,6].

1. RAFAKO S.A. IMPLEMENTATION PROGRAM OF NEW CREEP-RESISTING STEEL GRADES WITH 9-12%Cr CONTENTS AND TUNGSTEN ADDITION

RAFAKO S.A. is a leading European manufacturer [10] of boiler pressure elements including heat membrane walls, boiler drums, coils, steam collectors and heat exchangers using all types of creep-resisting steel grades - including creep-resisting steel grades with 9 - 12% Cr contents and with addition of molybdenum, tungsten and cobalt - in fabrication of pressure parts. Construction of new power generating units in Poland combined with a growing share of RAFAKO export to European Union countries have forced the suppliers of boilers with supercritical parameters to implement the activities aiming at implementation of new generation creep-resisting steel grades for fabrication of coils and collectors of steam superheaters. It has also determined the scope of implementation of new creep-resistant steel grades due to RAFAKO participation in COST522 program.

RAFAKO S.A. implementation program of new creep-resisting steel grades with 9 - 12% Cr contents and with addition of molybdenum, tungsten and cobalt (as elements increasing both recrystallisation temperature and matrix stability during long-lasting operation in elevated temperature) included, among others, the following activities:

- steel weldability assessment on the basis of simulation of thermal cycles,
- correct selection of welding and heat treatment parameters, post-weld non-destructive testing,
- welded joint quality assessment on the basis of results of mechanical and process properties examinations carried out at ambient temperature and at elevated temperatures,
- assessment of low-cycle fatigue resistance as well as structural examinations of base material and weld joints carried out directly upon completion of welding and heat treatment and upon simulation of temperature conditions, which occur in operation of boiler superheaters.

Examinations were carried out on base material and both similar and dissimilar welded joints of coils made of HCM12, T122 (HCM12A), P92 as well as on sections of steam collectors made of P122 (HCM12A) and E911 steel grades delivered by Sumitomo and Vallourec within the framework of COST522 program.

Apart from steel weldability assessment the implementation program for welding process of similar and dissimilar welded joints also included the assessment of structure, strength and process properties including:

- non-destructive testing in accordance with design (customer's) documentation requirements,
- assessment of strength properties: R_m, R_{0.2} and HV,
- macro- and microstructure examination of HAZ, weld deposit and welded joints,
- impact resistance assessment carried out on V-notch samples,
- bend testing (bending angle:180°),
- fatigue examination for the low number of cycles,
- assessment of structural changes occurring in base material and in welded joints during the simulation of operational temperature of steam superheater elements [6,7],
- assessment of structural changes occurring in base material and in welded joints during 20.000 hours of operation in actual boiler operating conditions of the boiler no. 7 in Belchatów Power Plant[9].

Assessment of strength and process properties as well as assessment of the structure of new creep-resisting, martensitic steel grades with tungsten addition were carried out in parallel in RAFAKO S.A. and in Silesian Technical University (Katowice) on selected welded joints of boiler superheater elements.

2. MATERIAL AND SCOPE OF EXAMINATIONS

Examinations were carried out martensitic steel grades containing 9 and 12%Cr with tungsten addition such as P92, HCM12 and HCM12A. Material subject to testing, i.e. elements made of new generation creep-resisting steel grades with the following dimensions:

- $\phi 38 \times 4$ mm made of HCM12 steel grade from Sumitomo,
- ϕ 38 × 6,3 mm made of T122 (HCM12A) steel grade from Sumitomo,
- $\phi 38 \times 6$ mm made of T92 steel grade from Valourec,
- ϕ 355 × 45 mm made of P122 (HCM12A) steel grade from Sumitomo

Specification of chemical composition of steel grades subject to examinations is shown in table 1.

Table 1. Specification of chemical composition of steel grades - in accordance with the requirements of standards – "norm" (upper lines of chemical composition) and specification of chemical analyses of tubes on the basis of data originating form material certificates (lower lines of chemical composition)[6].

Steel grade			Contents [%]													
		С	Si	Mn	Р	S	Ni	Cr	Mo	W	Cu	V	Nb	Al	В	Ν
	Norm	0,07		0,3				8,5	0,3			0,15	0,04		0,001	0,03
		÷	<0.5	<0.5 ÷	<0,02	2 < 0,01	<0,4	÷	÷	1,5÷2	-	÷	÷ <0,04	÷	÷	
92		0,13	~0,3	0,8				9,5	0,6			0,25	0,09)	0,006	0,07
Å.	Cert.	0,094	0,21	0,46	0,015	0,002	0,26	8,84	0,47	1,72	-	0,21	0,07	0,04	0,038	0,06
HCM12	Norm	<0,14	<0,5	0,3 ÷ 0,7	<0,03	<0,03	-	11 ÷ 13	0,8 ÷ 1,2	0,8 ÷ 1,2	-	0,2 ÷ 0,3	<0,2	-	-	-
	Cert.	0,1	0,26	0,53	0,028	0,02	-	11,93	1,01	1,02	-	0,24	0,04	-	-	-

T122 (HCM12A)	Norm	0,07 ÷ 0,14	<0,5	<0,7	<0,02	<0,01	<0,5	10 ÷ 12,5	0,25 ÷ 0,6	1,5 ÷ 0,3	0,3 ÷ 1,7	0,15 ÷ 0,1	0,04 ÷ 0,1	<0,04	< 0,005	0,04 ÷ 0,1
	Cert.	0,13	0,31	0,6	0,014	0,001	0,35	10,65	0,35	1,92	0,94	0,22	0,06	0,009	0,0009	0,061
16d	Norm	0,08 ÷ 0,12	0,2 ÷ 0,5	0,3 ÷ 0,6	<0,02	<0,01	<0,4	8,0 ÷ 9,5	0,85 ÷ 1,05	-	-	0,18 ÷ 0,25	0,06 ÷ 0,1	<0,04	-	0,03 ÷ 0,07
	Cert.	0,10	0,45	0,44	0,015	0,001	0,13	8,16	0,94	-	-	0,21	0,07	0,04	-	0,06

Due to the limited space available this article shows only the selected results of strength and metallographic examinations within the field of assessment of base material properties and structure stability in both similar and dissimilar joints of welded joints of steam superheater coils elements made of HCM12, T122 (HCM12A) and P92 steel grades:

- after welding and heat treatment,
- after annealing simulating actual steam superheater operating conditions,
- after 20.000 hours of operation in actual operating conditions of boiler no. 7 in **Belchatów Power Plant.**

3. RESULS OF MICROSTRUCTURE AND HARDNESS DISTRIBUTON OF 9 AND 12%Cr STEAL GRADE IN DELIVERY CONDITION AND AFTER WELDIND AND **HEAT TREATMENT**

3.1 P92 steel grade

The structure of P92 steel grade in delivery condition includes tempered martensite of slat structure (fig. 1a, b). Areas of $M_{23}C_6$ and MX were detected - they are visible at the limits of δ ferrite grains and primary austenite grains as well as at the limits of martensite slats (fig. 1b). Measured steel hardness amounts to c.a. 225 HV and its impact resistance equals kV~145 J/cm²[8].



Fig.1a. P92 steel grade - tempered martensite Fig.1b. P92 steel grade - detail of structure of slat structure LM, magn. 500×



from fig. 1a. δ Ferrite areas in martensitic SEM matrix, magn. 470×

3.2 T122 (HCM12A) steel grade

T122 (HCM12A) steel grade in delivery condition after normalisation at a temperature of 1050°C / 60min. and tempering at a temperature of 750°C / 60min. show a tempered martensite structure with a small amount of δ ferrite (c.a. 3%) and release of M₂₃C₆ carbides, within the area of tempered martensite grains and at the limits of martensite slats (fig. 2a, b). Measured hardness of examined material ranges from 260 to 265 HV[4,6].



a) LM magn.150×

b) SEM magn. 3000×

Fig. 2. T122 (HCM12A) steel grade microstructure after austenitisation at a temperature of 1050° C / 60min and tempering at a temperature of 750° C / 60min. Tempered martensite with ferrite δ .

All of the joints have been welded at RAFAKO SA The tube joints $\phi 38 \times 6.3$ mm were TIG welded using T-HCM12A $\phi 1.6$ mm Sumitomo wire with a preheating temperature of 250 °C. For welding pipe joints $\phi 355 \times 45$ mm the same wire was used for the root pass (TIG) and Sumitomo stick electrodes HCM12A $\phi 2.4$ and $\phi 4.0$ mm – for filling passes. Welded joints were heat treated for 5 h at the temperature of 740 °C (tubes) and 760 °C (pipe).

Macrostructure of tube welded joints, measured hardness and hardness distribution of joint ϕ 38 x 6,3 mm is presented in Fig. 3.





HAZ

Weld deposit A

Fig 3. Microstructure, measured hardness and hardness distribution of weld T122 (HCM12A-T-HCM12A -HCM12A) steel grade

4. RESULTS OF MICROSTRUCTURE EXAMINATIONS OF STEEL GRADES WITH 9 AND 12% Cr AFTER ANNEALING SIMULATING ACTUAL OPERATING CONDITIONS

The purpose of the assessment of steel grades behaviour in actual boiler operating conditions, i.e. after ~100.000 hours, selected welded joints were subject - in RAFAKO S.A. - to strength examinations and structure assessment after simulation annealing (steel ageing) at a temperature of 700 °C during the period from 100 to 1000h.

Steel grades subject to annealing simulating the long-lasting operation of steam superheater in actual boiler operating condition show the tempered martensite structure with release of partly coagulated $M_{23}C_6$ carbides. The annealing process has also resulted in the increase of released carbide phases when compared with delivery condition.

4.1 P92 steel grade

P92 steel grade after long-lasting annealing shows coarse needled martensite structure with deltaferrite areas. Release of coagulated carbides forms a characteristic grid at the limits of δ ferrite islands (fig. 4a, b).



Fig. 4a. P92 steel grade structure after simulation annealing. Tempered martensite. LM magn. 500×



Carbide release was also observed at the limits of martensite slats (fig. 4a). Phase composition examinations have shown the following phases: $M_{23}C_6$, MX, M_2X and Laves phase. Increased amount of release is supported by $M_{23}C_6$ carbide coagulation process and release of large Laves phase particles (fig. 4a, b). Measured hardness of examined material ranges from 200 to 210 HV and its impact resistance measured on kV samples amounted to c.a. 75 J/cm².

4.2 T122 (HCM12A) steel grade

Structure of steel after annealing at a temperature of 700 °C / 200h is shown on fig. 5a, b. Simulation annealing triggers the processes of accelerated carbide release and further spheroidising. Structure of steel shows increased size of carbide released at grain limits and diversified dislocation density.



a)LM, magn. $650 \times$ b) SEM, magn. $8000 \times$ Fig.5. T122 (HCM12A) steel grade structure after annealing at a temperature of 700 °C. Martensite with M₂₃C₆ carbide release at grain limits. Visible δ ferrite areas.

5. RESULTS OF EXAMINATIONS OF MICROSTRUCTURE AND PROPERTIES OF STEEL GRADES WITH 9 and 12% Cr CONTENTS AFTER c.a. 20 000 HOURS OF OPERATION IN ACTUAL OPERATING CONDITIONS

5.1 Assessment of mechanical properties of examined steel grades

Examined material consisted of steam superheater tubes made of HCM12, T122 (HCM12A) and T91 steel grades, with 38 mm diameter and wall thickness 4, 4 and 6,3 mm respectively. Analysed tubes were operated for c.a. 20 000 hours in a P3 superheater of boiler no. 7, type BB-1150 in Belchatów Power Plant. Examinations were carried out both at ambient temperature and at a temperature of 600°C. Results of examinations carried out at ambient temperature are shown in table 2, and results of those carried out at a temperature of 600°C are shown in table 3.

Steel grade	Sample no.	S _o [mm ²]	R _{0.2} [MPa]	R _m [MPa]	A ₅ [%]
HCM12	1	53,32	450	716	20,5
	la	53,53	454	691	21
(T122)	2	51,7	600	774	40
HCM12A	2a	58,05	503	651	22
P91	3	82,6	608	815	14,4
	3a	83,3	600	810	14,4

Table. 2. Results of welded joint static tensile test at ambient temperature.

Table no. 3. Results of welded joint static tensile test at a temperature of 600°C.

Steel grade	Sample no.	S _o [mm ²]	R _{0.2} [MPa]
HCM12	1	50,74	244
	1a	51,6	262
T122 (HCM12A)	2	56,4	277
	2a	56,4	291
P91	3	77,7	286

6. ASSESSMENT OF MICROSTRUCTURE EXAMINATIONS RESULTS OF STEEL GRADES WITH 9 and 12% Cr CONTENTS AFTER c.a. 20 000 HOURS OF OPERATIONS IN ACTUAL BOILER OPERATING CONDITIONS

6.1 T122 (HCM12A) steel grade after 20 000 hours of operation shows a tempered martensite structure with a small amount of δ ferrite (<5%). Few M₂₃C₆ carbide releases were observed at grain limits (fig. 6a, b, c, d). Measured hardness of material reaches the level of 223 HV.





Fig. 6. T122 (HCM12A) steel grade microstructure after 20 000 hours of operation. LM, SEM.

T122 (HCM12A) steel grade substructure after 20 000 hours of operation shows well-formed polygonal sub-grains (fig. 6a), inside which we observe a very low dislocation density - result of combined temperature and time effect. We also observe the release of $M_{23}C_6$ carbide, mainly at the limits of equiaxial sub-grains (fig. 7b, c, d). Released carbides have characteristic elongated and coagulated form. At the vicinity of coagulated $M_{23}C_6$ carbides we observe the elongated Laves phase particles (fig. 7e, f). However, the occurrence of such phases is rarely seen and frequently such elongated releases are $M_{23}C_6$ carbide particles. MX -type release occur inside sub-grains.



a)	Sub-granular	structure	with	numerous	b) Diversified morphology of $M_{23}C_6$ release.				
car	bide release at	limits.			Magn. 17000x				
Ma	gn. 6700x								



e) M₂₃C₆ carbide release (fig. 2) in HCM12A f) T122 (HCM12A) material diffraction from steel grade. Light field. Magn. 33000x fig. 2.

Fig. 7. T122 (HCM12A) steel grade sub-structure after 20 000 hours of operation, TEM analysis.

7. SUMMARY AND CONCLUSIONS

During the mechanical examinations it was clearly stated that the lowest yield point - both at ambient temperature and at a temperature of 600° C - is characteristic for HCM12 steel grade. P91 and T122 (HCM12A) steel grades have similar yield point and tensile strength values, not depending on the temperature of examination (see tables 2 and 3), and similar A₅ elongation, which meet the required material properties level expected during boiler operation process.

P92 steel grade in delivery condition has a characteristic tempered slat martensite structure with δ ferrite areas and M₂₃C₆ carbide release. Sub-structure shows the elongated arrangements of tempered martensite sub-grains with high dislocation density as well as M₂₃C₆ and MX carbide release at the limits and inside the sub-grains. Material hardness reaches the level of 225 HV and impact strength amounting to ~145 J/cm².

After long-lasting annealing (annealing simulating boiler operating conditions), P92 steel grade shows a coarse-needled martensite structure with δ ferrite areas. Release of coagulated carbides form a characteristic grid at the limits of δ ferrite islands. In a sub-structure we observe a very intensive processes of recovery and traversing as well as increase of number and size of carbide release. Polygonal sub-grains are dislocation-free. Phase composition examinations have shown the occurrence of M₂₃C₆, MX, M₂X release and Laves phase. Measured steel hardness of 200 HV is

lower than in delivery condition whereas the impact resistance on kV samples amounted to \sim 75 J/cm². Completed examinations demonstrate that P92 steel grade is also characterised with satisfactory structure and property stability, which is however lower than in case of E911 steel grade.

T122 (HCM12A) steel grade in delivery condition shows tempered martensite with low number (c.a. 5%) of δ ferrite and few M₂₃C₆ carbide release at the limits of martensite grains and blocks as well as MX release inside said blocks. Measured hardness of examined material in delivery condition is slightly higher - by c.a. 40 HV - when compared with T12 (HCM12) steel grade and amounts to 263 HV. Impact resistance measured on kV samples amounts to ~95 J/cm².

After annealing at a temperature of 700° C / 100h, the structure of HCM12A steel grade demonstrates the increase of the size of carbides released at grain limits as well as diversified dislocation density when compared with delivery condition. After annealing at a temperature of 700° C / 200h this process is further continued with clear coagulation of carbide released at the limits of primary austenite grains. It was also demonstrated that the processes of accelerated cabide release and further spheroidising occur due to the annealing. Steel hardness is lower - when compared with delivery conditions - and amounts to 232 HV. Completed examinations demonstrate that HCM12A steel grade is characterised with relatively high stability of structure and properties.

T122 (HCM12A) steel grade after c.a. 20 000 hours of operation shows a tempered martensite structure with low δ ferrite contents (<5%). Moreover, few M₂₃C₆ carbide release were observed at grain limits. Sub-structure is characterised with well-formed polygonal sub-grains, inside which we observe a low dislocation density resulting from combined temperature and time effect. M₂₃C₆ carbide release were observed mainly at the limits of equiaxial sub-grains. Released carbides have a characteristic elongated and coagulated form. MX-type release occur inside the sub-grains. Material hardness amounts to 223 HV.

In authors opinion, the selection of simulation annealing parameters at the level of 700° C during 100 - 1000 hours assures the temperature conditions enabled the correct assessment of steel behaviour and steel properties level - such as e.g. strength properties stability or steel structure stability - in conditions reflecting c.a. 100 000 hours of boiler operation.

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