DEVELOPMENT OF NEW STRUCTURAL WEATHERING STEELS

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Abstract

The steels with increased atmospheric corrosion resistance ï weathering steels are profitably employed for traffic ways and railways steel structures (especially bridges). Against to atmospheric corrosion these steels are protected by self formation of stable oxide layer ï patina. Structures made of these steels need not anticorrosive protective coating, which is their economical and ecological advantage.

Weathering steels most widely produced in Czech Republic correspond to grade 15127 according to the former ĻSN standards. According to ĻSN EN 10025-5 the conforming grade is S355J2W. Chemical composition of this steel in both standards respects wide thickness range to 150 mm, material status after classical normalization and presently out of date level of metallurgical processes. Some alloying elements content, including carbon, is rather high at production of grade 15127. Carbon equivalent of these steels is on the top limit of CE_{IIW} = 0,52% due to this rather high alloying, together with only moderate atmospheric corrosion resistance (evaluated by corrosion resistance index CRI based on ASTM G101 standard).

Modified alloying conceptions of this weathering steel standard were suggested on the basis of literature retrieval and by virtue of computer simulation in TTSteel software. These modified alloying conceptions include low-carbon microalloyed steel, low-carbon steel with increased Si and Al content and high strength bainite air-quenched steel. The work presents mechanical properties of experimental steels determined via computer simulation in comparison with mechanical properties measured on industrial normalization rolled flanges from experimental semi-industrial heats. Moreover, based on the computer simulations, thermomechanical rolling concept for improvement of mechanical properties of these steels is presented.

Key words: Atmofix, weathering steel, corrosion, micro-alloyed steel, thermomechanical processing, microstructure

1. Introduction

The expenditure of steels for traffic and railroad bridges that donőt require protective paint or other coating increases presently especially abroad. Lower ecological stress and cost savings are the main reasons. Basic specific feature of steels with increased atmospheric corrosion resistance (weathering steels) are their ability to stepwise rust layer creation at proper atmospheric conditions. The rust layer significantly decrease corrosion rate. First weathering steel was patented and established at 1933 in USA. Steels marked Atmofix were developed in ĻSSR in period after 1968. These steels were comparable to steels Corten by their properties.

Several tens of objects were built subsequently; main representative of these objects have been periodically evaluated. The masts and bridges structures are the most often utilization of these steels.

Demands of high-strength weathering steels for exacting structures rise too. Especially the Atmofix brand steels of grade S235W(P) and S355W(P) (according to the standard ĻSN EN 10025-5) are employed mostly for traffic and railroad bridges in ĻR. These weathering low-alloyed steels contain small amount of Cr, Cu, Ni, P and other elements (e.g. Mo). Their microstructure is ferrite-pearlite and they have yield strength to about $R_{p0,2}$ = 400MPa and real elongation value above A5 = 30% and they have rather good corrosion resistance CRI = 6,2÷6,5 (corrosion index according to the standard ASTM G101). Although the properties are sufficient for ordinary (less exacting) structures, this ferrite-pearlite concept of weathering steels has no more potential for another development from metallurgical and material point of view. **Fig. 1.** shows TTT diagram of weathering steel S355J2W constructed via computer simulation in software TTSteel for more detail approach on this steel.

Worldwide development of high-strength steels with enhanced atmosphere corrosion resistance have been raised by constructions of exacting traffic and railroad bridges in coastal areas with increased chloride content in atmosphere (increased salinity). Concept of weathering steel with increased Ni content (to 3% wt. Ni) was developed several years ago. However higher Ni content essentially increase cost of steel and embarrass its recycling. These are the main reasons for partial leaving this alloying concept. Based on thermodynamical stability analysis of various corrosion patterns (Fe-X systems) it was determined that in metallurgy common elements Si and Al have potential to create stable complex oxides with Fe. Moreover Si and Al havenôt negative influence on steel recycling. No mater about Si and Al content in steel itôs known the strength increase could be acquired by grain refinement.

Hence worldwide microalloyed thermomechanically rolled steels with ferrite-pearlite microstructure are one of the fundamental trends in high-strength steels with enhanced atmosphere corrosion resistance development. Low-alloyed bainite (eventually ferrite-bainite) weathering steels are another one of present trends in development of high-strength steels with enhanced atmosphere corrosion resistance.

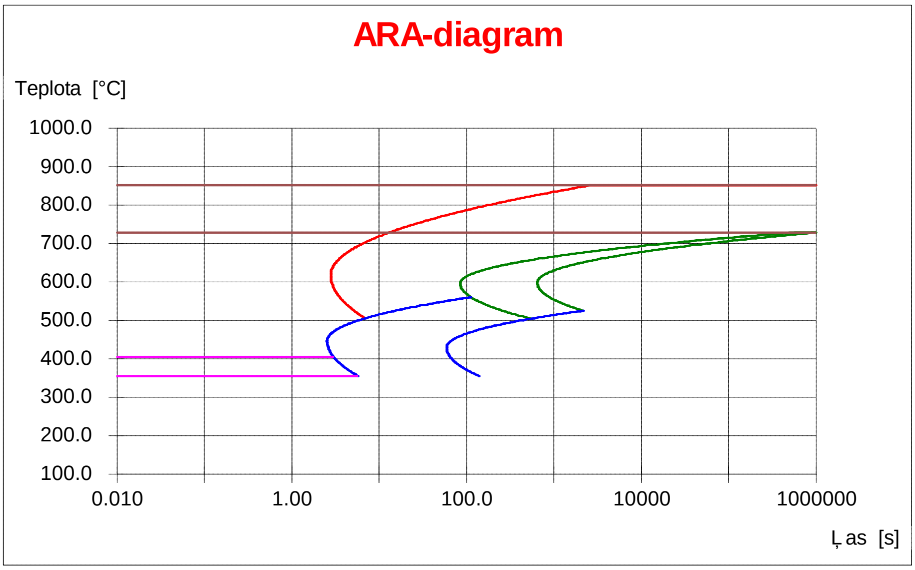


Fig. 1. Computer simulation of weathering steel S355J2W TTT diagram

1.1 Microalloyed thermomechanically rolled steels

Micro-alloyed steels are low carbon steels with classic ferrite-pearlite microstructure. Number of authors have studied alloying elements influence [e.g. 2-4], corrosion layer structure [e.g. 5-7] and another corrosion properties/behaviors. Zhang [8] indicates that pearlite in weathering steel 09CuPCrNi deteriorate corrosion resistance (determined at accelerated corrosion test in synthetic salt spray). Chen [9] studied low-carbon microalloyed steels with various microstructures (pure ferrite, ferrite- pearlite and ferrite-bainite). Although the results weren't fully clear (due to employed procedure) the lowest corrosion resistance showed steel with ferrite-pearlite microstructure. Formation of pearlite phase is strongly restricted due to specific chemical composition at microalloyed thermomechanically rolled steels. Extraordinary mechanical properties are acquired at these steels by virtue of fine-grained microstructure. This microstructure is result of microalloying, eventually in combination with suitable thermomechanical processing. E.g. Nishimura [10] in his work quenched slab from temperature 1100°C to 650°C. In temperature interval 650°C to 500°C he subsequently carried multi-pass hot rolling with total strain 95%. This way he acquired ultrafine-grained microstructure consisted of ferrite and cementite. Grain size of sample rolled at 600°C was 1μm – see **Fig. 2.** It is in principle same grain size like at ordinary carbon Si-Mn steel rolled at identical temperature. However ultimate strength of micro-alloyed steel with Si and Al was 130MPa higher than ultimate strength of carbon Si-Mn steel. It is the effect of solid solution strengthening through Si and Al. Generally could have been told that steel with Si and Al shows lower elongation in comparison with Si-Mn steel. However due to grain refinement rolled samples from micro-alloyed steel with Si and Al exhibit extraordinary high elongation. Based on this findings development of steel with increased Si and Al content to the achievement of higher corrosion resistance and very good elongation due to grain refinement seems to be hopeful .

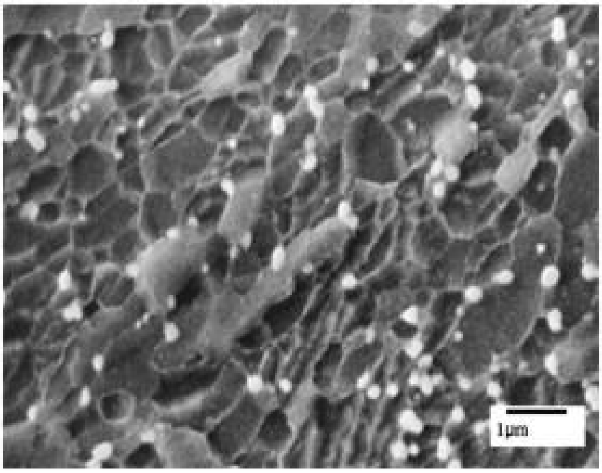


Fig. 2. Microstructure of microalloyed steel with Si and Al after rolling at temperature 600°C [10]

1.2 Low carbon bainite steels

In comparison with classic ferrite-pearlite weathering steel they exhibit higher strength due to bainite microstructure and excellent weldability due to low carbon content. Low carbon content affects formation of homogeny bainite too. Strength decrease as the result of low carbon content has to be compensated by suitable alloying (microalloying) and thermomechanical processing. Homogeny bainite fraction in microstructure induces very good atmosphere corrosion resistance in addition to extraordinary mechanical properties according to various authors [e.g. 9]. Thermomechanical processing constitutes of rolling with subsequent accelerated cooling for classic bainite steels. Microstructures of these classic bainite steels are presented on **Fig. 3.** (**Fig. 3a** ï steel with 0,03% wh. of C; **Fig. 3b** ï steel with 0,05% wh. of C). Both steel microstructures are similar; they mainly consist of granular bainite (GB) and bainitic ferrite (BF) with small amount of acicular ferrite (AF).

However certain issues appear along this alloying concept employing or generally along bainite steels employing as steels with enhanced atmosphere corrosion resistance. From principles bainite weathering steel isnôt already able to comply fully with limits of standard ĻSN EN 10025-5. This way framed steel accelerated cooled after rolling doesnôt respond to delivery conditions provided by standard beyond chemical composition limits exceeding. Standard ĻSN EN 10025-5 provides only delivery condition +N (normalization annealing or normalization rolling) or +AR (after rolling) for heavy plates. This problem would be possibly solvable by material specification based delivering. However matter of restraint is that traditional Czech producer of weathering steel plates doesnôt possess technology for plates accelerated cooling since. At chemical composition under consideration the plate microstructure would consist of ferrite and pearlite with only minimal bainite volume fraction (eventually without any bainite) after free air cooling of plate second to rolling. We are attempting to adjust bainite weathering steel chemical composition in frame of project *MPO FT-TA5/076 ï Study of existing and newly developed weathering steels in respect to their usage for steel structures* treatment. The experiments are headed to development of self-quenching bainite weathering steel.

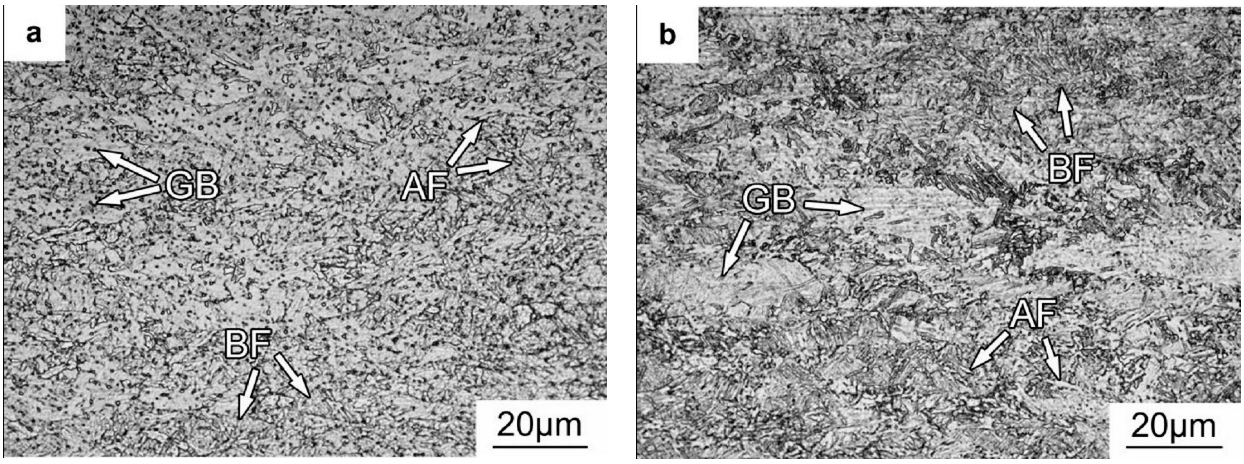


Fig. 3. Weathering steels microstructureï **a)** steel A1 with 0,03%C ï quasi-polygonal ferrite, granular bainite and bainitic ferrite; **b)** steel A2 with 0,05%C ï granular bainite, bainitic ferrite and little bit of acicular ferrite [4]

2. Experiment description

Need of increased corrosion resistance in environment with higher salinity (or in context of increased salt scattering) was mentioned in introduction. We took into account modern worldwide evolutionary concepts of steels with enhance corrosion resistance. However chemical compositions of both microalloyed thermomechanically rolled and low-carbon bainite steels were modified to get near standard ČSN EN10025-5 limits and production and technological abilities.

Software TTSteel was employed as a support tool for these chemical composition modifications. TTSteel is software for construction of transformation diagrams and mechanical properties prediction of steel after their thermal treatment. These properties are simulated by virtue of chemical composition and initial austenite grain structure.

Chemical compositions of microalloyed thermomechanically rolled steels were modified especially to get near standard ČSN EN10025-5 limits. Deteriorative influence of pearlite phase on corrosion resistance was mentioned in introduction. Two different modifications of microalloyed weathering steels were suggested. These steels have strongly restricted pearlite phase due to specific chemical composition. The first one steel has reasonably increased (to the ČSN EN 10025-5 standard top limits) Si and P content. The second one microalloyed steel has significantly increased Si and Al content. These elements ability to compose stable oxides increasing corrosion resistance was mentioned. Exact chemical compositions of both semi-industrial heats of microalloyed weathering steels are given in **Table 1.**

Chemical composition of low-carbon bainite steel has to be modified for bainite phase achievement in microstructure at cooling rate equal to free air cooling. Significant increase in B alloying level was carried out together with partly increased Mn, Ni and Mo content for the reason. Carbon equivalent of steel has increased in consequence of this, however still suit to limit CE_{max} = 0,52 for grade S355 due to standard ČSN EN 10025-5. Exact chemical composition of semi-industrial heat of low-carbon bainite weathering steel is given in **Table 1.** too.

Tabulka 1. Chemického složení poloprovozních taveb patinujících ocelí

Element content [% wh.]	Heat marking		
	Microalloyed	Si + Al	Bainite
C	0,05	0,08	0,05
Mn	0,9	1,2	1,9
Si	0,5	0,7	0,3
P	0,03	0,01	0,01
S	0,005	0,005	0,005
Ni	0,01	0,01	0,2
Cr	0,55	0,2	0,4
Mo	0,005	0,005	0,05
Cu	0,3	0,3	0,3
V	0,005	0,005	0,008
Ti	0,019	0,019	0,019
Nb	0,05	0,05	0,05
Al	0,05	0,7	0,05
B	0,0003	-	0,003
CEV [%]	0,333	0,343	0,492
CRI [-]	6,735	6,270	6,218

The corrosion index CRI values characterizing corrosion resistance of steel are introduced in **Table 1.** too. However these are estimative values only for steels with these alloying concepts. According to standard ASTM G101 corrosion index CRI was defined based on corrosion resistance results of steels with slightly different chemical composition (e.g. CRI doesnôt reflect elements like Si and Al).

Semi-industrial heats were cast at temperature cca 1620°C into ingots 15HE, the ingots weight were about 1400kg. All three ingots were rolled on blooming mill for slabs with cross section dimensions 135x250mm. Subsequently the slabs were rolled on universal rolling mill type of Lauth three-high mill for flanges with thickness 10mm; 20mm and 35mm. Finishing rolling temperatures for single thicknesses were 890°; 860°C and 850°C.

3. Measured values and evaluations

Mechanical properties (proof stress $R_{p0,2}$, ultimate strength R_m and elongation A5) of single flanges from all semi-industrial heats in conditions after normalization rolling were determinate by tension test on full thickness flat samples 10mm; 20mm and 35 mm (see **Fig. 4.** ï flat samples after fracture). Mechanical values stated in flanges rolling direction (longitudinal direction in term of flat products testing) are introduced in **Table 2.** Itôs noticeable that for all three thickness of all three semi-industrial heats high level of proof stresses were acquired (all values fulfill requirements of standard ĻSN EN 10025-5 for grade S355). As for ultimate strength the maximal ultimate strength limit given by standard was exceeded at bainite weathering steel concept. Elongation values are on extraordinary high level (for grade S355), especially at steels marked ñMicroalloyedò and ñSi+Alò. At ñBainiteò steel elongation is somewhat lower, however in view of steel strength elongation doesnôt dramatically drop under requested level for grade S355 according to standard ĻSN EN 10025-5.

Fig. 4. Tension tests flat samples with thickness 10, 20 and 35 mm after fracture

Table 2. Tension test results of 3 semi-industrial weathering steel heats

Flange thickness [mm]	Microalloyed			Si + Al			Bainite		
	$R_{p0,2}$ [MPa]	R_m [MPa]	A5 [%]	$R_{p0,2}$ [MPa]	R_m [MPa]	A5 [%]	$R_{p0,2}$ [MPa]	R_m [MPa]	A5 [%]
10	410	544	29,5	460	555	32,0	422	678	21,4
20	397	486	33,3	443	535	31,4	405	650	24,6
35	369	485	29,3	402	525	27,5	403	656	20,4

Standard Ų SN EN 10025-5 features minimal yield strength R_{emin} = 355MPa, ultimate strength R_m = 470÷630MPa and minimal longitudinal elongation A5 = 22% for plates with thickness under 40mm.

Properties of flanges with thickness 20mm with chemical composition equal to semi-industrial heats ñMicroalloyedñ and ñBainiteñ predicted via computer simulation in software TTSteel are introduced in **Table 3.** Featured properties are results of free air cooling simulation of flanges with thickness 20mm after rolling with finish rolling temperature 860°C. Cooling simulation wasnôt undertaken for steel with chemical composition equal to semi-industrial heat ñSi+Alò since too high Si and Al content exceed range of calculating mathematical algorithm of TTSteel software.

Table 3. Semi-industrial heats of weathering steels properties determined by computer simulation

Properties	Heat marking	
	Microalloyed	Bainite
HV/HB/HRC	164/170/16	259/243/23
Yield strength R_e [MPa]	293	525
Ultimate strength R_m [MPa]	485	761
Elongation A5 [%]	35	12
Transit temperature [°C]	- 47	24
Structure	96,2% F/ 3,8% P	44,5% F/ 55,5% B
A_{C3} [°C]	892	867
A_{C1} [°C]	739	717
A_{R3} [°C]	829	672

Comparison of mechanical proprieties of ñMicroalloyedñ semi-industrial heat determined via real tension tests and computer simulation exhibit very good agreement at strength values and values of elongation. Yield strength value determined through computer simulation is lower than value determined though real tension test that is unfortunately typical for TTSteel software at microalloyed steels. We didnôt expect special accuracy at mechanical properties computer prediction of low-carbon bainite steel (cause of mechanical properties prediction for self-quenching steels with relatively simple mathematical algorithm like e.g. TTSteel uses is estimative only) so that we consider relation of yield strength and ultimate strength values determined via real tension tests and computer simulation as good. However real tension test determined elongation value is surprising for bainite steel.

Fig. 5. and **Fig. 6.** illustrate computer simulation of TTT transformation diagrams for chemical composition equal to semi-industrial heats “Microalloyed” and “Bainite” Into both steels TTT transformation diagrams were inserted cooling curves representing free air cooling of 20mm thick flanges.

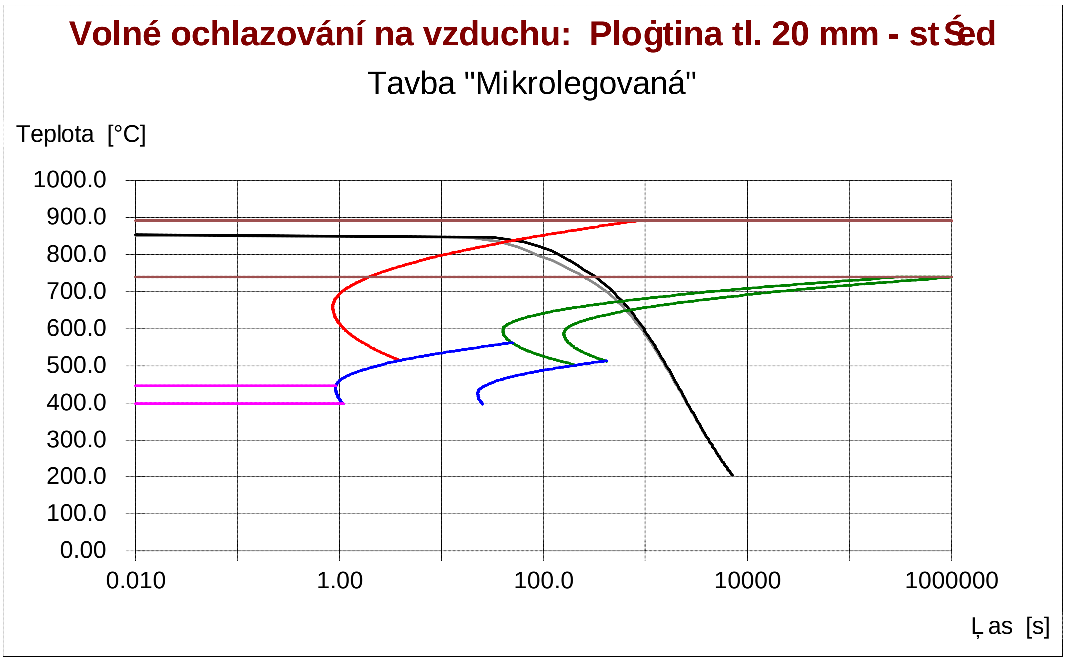


Fig. 5. Computer simulation of microalloyed weathering steel semi-industrial heat TTT diagram with inserted free air cooling curve of 20 mm thick flange

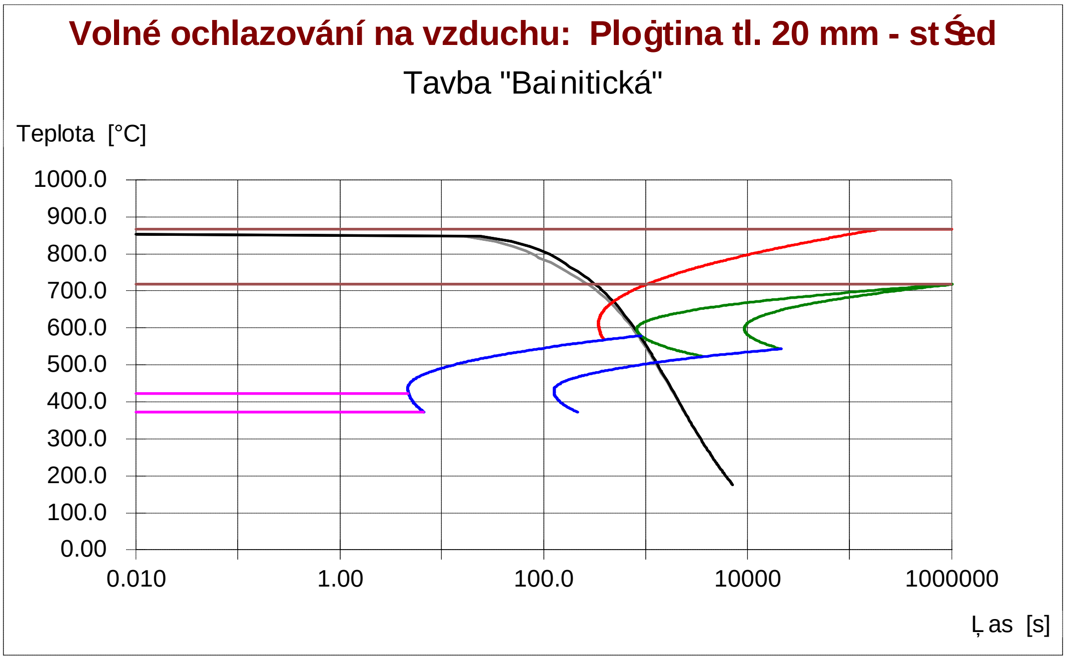
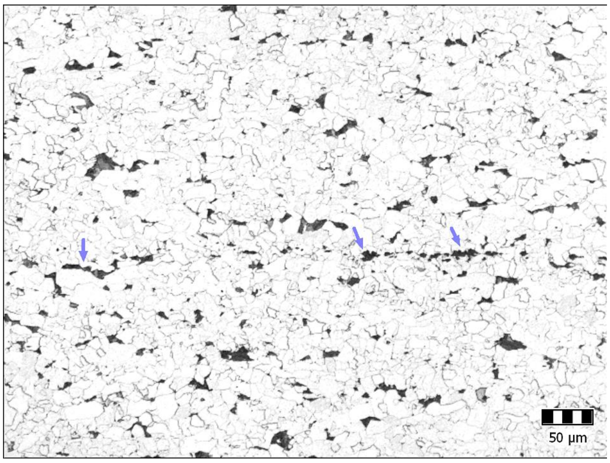


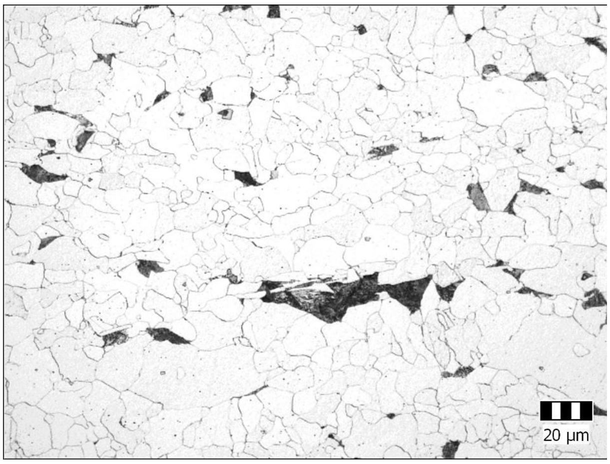
Fig. 6. Computer simulation of bainitic weathering steel semi-industrial heat TTT diagram with inserted free air cooling curve of 20 mm thick flange

Microstructure investigation and providing of single phases volume fractions were carried out on samples from 20mm thick flanges of all three semi-industrial weathering steels heats. Classical metallographic preparation is composed of grinding, sanding and etching in Nital. Microstructure images with magnification 200x, 500x and 1000x were acquired on microscope OLYMPUS with CCD camera.

Fig. 7. illustrates microstructure from ½ of flange thickness from "Microalloyed" weathering steel. Oxide lines in ferrite phase (indicated by arrow-heads on image with magnification 200x) are results of semi-industrial heats processing and could be passed away. Microstructure of "Microalloyed" weathering steel is ferrite-pearlite with slight orientation in rolling direction and strongly reduced pearlite phase.

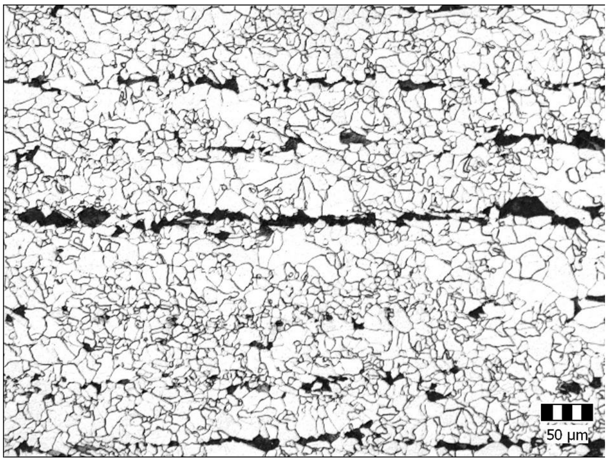


Magnification 200x

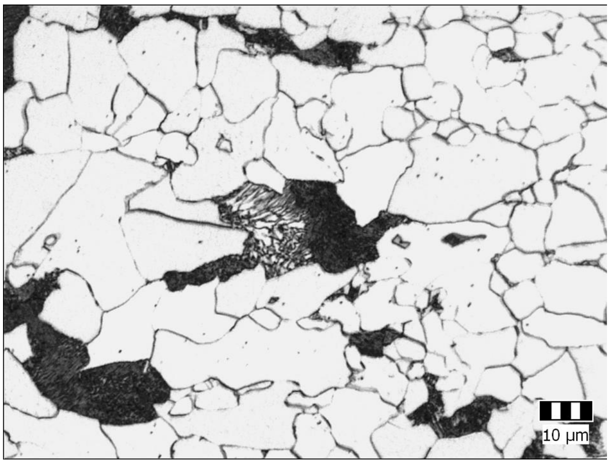


Magnification 500x

Fig. 7. Microstructure of microalloyed semi-industrial weathering steel heat (image from ½ of flange thickness)



Magnification 200x



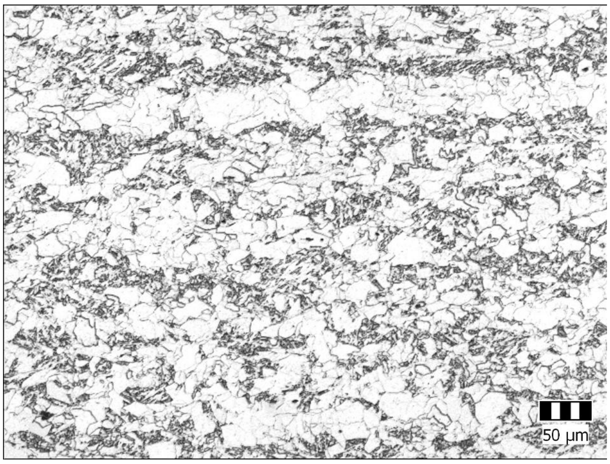
Magnification 1000x

Fig. 8. Microstructure of microalloyed semi-industrial weathering steel heat with high Si and Al content (image from ½ of flange thickness)

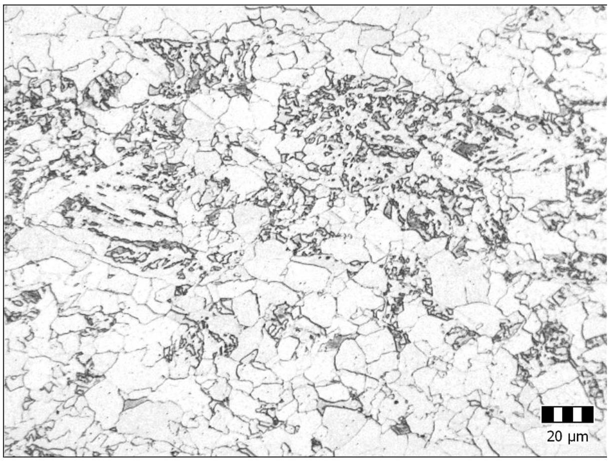
Fig. 8. illustrates ferrite-pearlite microstructure of "Si+Al" weathering steel (with reduced pearlite volume fraction) with magnification 200x and 1000x. Microstructure is look-alike to microstructure of "Microalloyed" weathering steel. Coarser oxide

inclusions and incoherent pearlite lines are results especially of semi-industrial heats processing again. Carbo-nitrides of titanium were detected on certain images.

Fig. 9. illustrates ferrite-bainite microstructure of ñBaniteñ weathering steel. Microstructure is slightly orientated in rolling direction. Image with magnification 500x is from ½ of flange thickness.



Magnification 200x



Magnification 500x

Fig. 9. Microstructure of bainitic semi-industrial weathering steel heat (image from ½ of flange thickness)

Volume fraction analysis of single samples was carried out by punctual method on ELTINOR 1000 instrument in approx. 1000 points. Resulting volume fractions values of detected phases are introduced in **Table 4.** Real detected values of volume fraction for ñMicroalloyedò and ñBainiteò weathering steel could be compared with values sat via computer simulation in TTSteel software (see **Table 3.** and **Table 4.**) Comparison shows nearly full agreement for ñMicroalloyedò weathering steel. Phase volume fraction computer prediction accuracy for low-carbon bainite weathering steel is very good too.

Table 4. Examined phases volume fraction (determined by point method)

Phase volume fraction [% vol.]	Heat marking		
	Microalloyed	Si + Al	Bainite
Ferrite	96,22	95,14	59,31
Pearlite	3,78	4,86	ï
Bainite	ï	ï	40,69

4. Conclusions

Principal characteristics and potential utilization of steels with enhance corrosion resistance are suggested in the work. Although the most applied weathering steels in Czech Republic are the Atmofix brand steels worldwide weathering steel progression tends to utilization of cheaper alloying concepts and modern rolling technologies. In the framework of research project on the basis of literature retrieval we consider possibilities of weathering steel chemical composition modification in trend of modern worldwide evolutionary concepts however to be workable at technically-technological conditions of traditional Czech producer of weathering steel plates and with respect to standard ĻSN EN10025-5 limits as much as possible.

Three semi-industrial heats of experimental weathering steel were made and subsequently rolled for flanges with this objective.

Very good mechanical properties of experimental flanges together with very good carbon equivalent value (CEV = 0,333% and CEV = 0,343%) were acquired at semi-industrial heats marked ñMicroalloedò and ñSi+Alò (for exact chemical composition see **Table 2.**) Microstructures of these weathering steels contain over 95% of ferrite what is presumption for high corrosion resistance. Another approach at these steels development is the rolling conditions. We tend to improve thermomechanical processing for further grain refinement and thereby mechanical properties improvement.

Higher bainite volume fraction (about 40% of bainite at flange with thickness 20mm) at free air cooled rolled flanges (therefore without accelerated cooling of flanges after rolling) was acquired by chemical composition modification. Ultimate strength of flanges from this steel is very high (reach to R_m = 660MPa ï in dependence on thickness) however yield strength is only average (proof stress values are about $R_{p0,2}$ = 410MPa). Low elongation value doubts werenÓt confirmed. Acquired elongation values are about A5 = 20%. However bainite fraction in microstructure is acquired for the price of higher alloying level so that carbon equivalent rise to value CEV = 0,492%. There are rather enough possibilities for next chemical composition modifications and for thermomechanical processing modification too at this steel. However low-carbon self-quenching bainite steel was acquired for examination of literature indications about very good corrosion resistance of bainite and ferrite-bainite steels.

In the framework of research project treatment another planned works on these steels development will include practical evaluation of steelÓs atmospheric corrosion resistance via accelerated cyclic laboratory test and even long-time corrosion resistance tests.

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