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# Influence of Heat Treatments and Ni Content on Properties of Martensitic Stainless Steel

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## Abstract

The article deals with the influence of chemical composition of martensitic stainless steel for castings GXCrNi13-4 (the 1.4317 material) on mechanical properties and structure of as cast steel after heat treatment. Properties of these martensitic stainless steel are heavily influenced by chemical composition and structure of the material after heat treatment. Structure of these steels after quenching is formed with martensite and residual austenite. When tempering the steel the carbon content in martensite is reduced and gently deposited carbides occur. The way of heat treatment has a major impact on structure of martensitic steels with low carbon content and thus on strength, hardness and elongation to fracture of these steels. Chemical composition of the melt has been treated to the desired composition of the lower, middle and upper bounds of the nickel content in the steel within the limits allowed by the standard. Test blocks were gradually cast from the melt. The influence of the nickel equivalent value on structure and properties of the 1.4317 steel was determined from results of mechanical tests.

**Keywords:** Stainless steels, Nickel equivalent, Mechanical properties, Structure, Volume of ferrite

## 1. Introduction

Martensitic stainless steels (MS) are very often used for the manufacture of castings intended for hydropower, such as castings of water turbines blades, impellers of pumps or pressure vessels. Martensitic steels with low carbon content where unique relationships between technological and mechanical properties and corrosion resistance of the material are achieved are particularly used for these purposes [1, 2]. Properties of these martensitic stainless steel are heavily influenced by chemical composition and structure of the material after heat treatment. Structure of these steels after quenching is formed with martensite and residual austenite. When tempering the steel the carbon

content in martensite is reduced and gently deposited carbides occur. The way of heat treatment has a major impact on structure of martensitic steels with low carbon content and thus on strength, hardness and elongation to fracture of these steels [3, 4] as well as the impact energy [5]. As reported by the authors of the work [5], it is important if the quenched structure of MS is tempered in one or more stages. The occurrence of ferrite in martensitic stainless steels is considered undesirable because according to some researchers the impact energy is reduced as a result of reduction of cohesion of ferrite with the surrounding matrix. On the other hand, the increase of the ferrite proportion leads to the growth of elongation to fracture. It was found in the work [6] that there has been a decrease of the impact energy of steel of the 13% Cr-4% Ni-Mo type at temperature of 0 °C from the value of around 210 J

(0% ferrite) to the value of around 105 J with the ferrite proportion of 7%. The carbon content in martensitic stainless steels is usually required low not only with regard to mechanical properties but also technological properties such as weldability. Low carbon content in steel reduces the occurrence of carbides in structure that also have a strong influence on the corrosion resistance, in particular the resistance to intergranular and pit corrosion. The work [7] describes an influence of heat treatment and the type of corrosive environment on the resistance of steel to corrosion and the thickness of the protective passivating layer. Chemical composition in individual phases in structure varies depending on heat treatment, which affects both the stability of individual phases of microstructure (residual austenite and ferrite), as well as the conditions of their transformation, e.g. the Ms and Mf temperature change [3–5]. With the choice of chemical composition within the range given by the standard and the used heat treatment it is possible to significantly influence the strength properties and ductility and toughness of the steel and to achieve optimal technological properties and corrosion resistance of the steel.

## 2. Experimental procedure

Chemical composition of the martensitic stainless steel GX4CrNi13-4 used for the production of parts of water turbines and composition of the steel planned for the experiment are given in Table 1. The maximum carbon content in the steel amounts to 0.06%. In the production of castings for hydropower from this type of steel the carbon content due to reclamation welding is often required in the range of only 0.01-0.02 weight %. Reduction of the carbon content by 0.04% (from 0.06% to 0.02%) will cause the change of the nickel equivalent by 1.2 – see the equation (1). The value of the chrome equivalent doesn't change with the change of the carbon and nickel contents.

$$Ni_{ekv.} = \%Ni + 0.5 \cdot \%Mn + 30 \cdot \%C + 30 \cdot \%N \quad (1)$$

$$Cr_{ekv.} = \%Cr + \%Mo + 1.5 \cdot \%Si + 0.5 \cdot \%Nb \quad (2)$$

The reduction of the  $Ni_{equi}$  can lead to an increase of the ferrite proportion in structure after processing the steel (the Schaeffler diagram) [1]. Some customers require the ferrite content in structure max. 2% or 5%. The change of carbon content (reduction of the nickel equivalent) should be compensated by increasing the nickel equivalent with adding the nickel so that the resulting ferrite proportion doesn't exceed the customer's requirement. Table 1 shows the range of the change of the nickel equivalent, which should occur by changing the Ni concentration in the steel. The chrome equivalent value for the planned chemical composition of steel is around 13.5.

Table 1

Chemical composition of steel

Element	Norm [wt. %]	Plan [wt. %]		
C max.	0.06	0.02		
Mn max.	1.00	0.80		
Si max.	1.00	0.40		
P max.	0.035	0.025		
S max.	0.025	0.005		
Cr	12.00-13.50	13.00		
Mo max.	0.70	0.20		
N	-	0.020		
Ni	3.50-5.00	3.5	4.2	5.0
$Ni_{equi}$	-	5.1	5.8	6.6

### 2.1. Production and processing of the metal

The steel was manufactured in an 80 kg vacuum medium-frequency induction furnace (VIF) with a neutral lining of the furnace Wedorit FM12. The planned weight of the melt was 79.2 kg. Reversible metal waste, non-alloy steel, was a basis of the charge. According to the results of the analysis of chemical composition of the metal charge it was additionally alloyed using FeCr, FeMo, FeSi and Ni. After melting the charge a sample was taken for testing the chemical composition and additional alloying of Ni for meeting the first analysis with the  $Ni_{equi}$  of 5.1. This was followed by vacuum treatment of the steel and with tapping temperature of 1690 °C the oxygen activity was measured and the first tapping into the casting ladle (CL) was carried out. First Y block weighing 19.5 kg was cast at the steel temperature in the CL of 1610 °C. The rest of the melt was poured from the CL into the furnace and the melt was additionally alloyed with Ni for achieving the second value of the  $Ni_{equi}$  of 5.8. After a brief vacuuming of the melt the oxygen activity was measured and at steel temperature of 1700 °C the second tapping into the CL was made. Second test Y block weighing 19.5 kg was cast at the metal temperature in the CL of 1602 °C. The rest of the melt was again poured back into the furnace and the melt was additionally alloyed with Ni for achieving the third value of the  $Ni_{equi}$  of 6.6. After a brief vacuuming of the melt the oxygen activity was measured and at bath temperature of 1670 °C the third tapping into the CL was made. Third test Y block weighing 19.5 kg was cast at the metal temperature in the CL of 1596 °C.

### 2.2. Manufacture of mould and pouring of castings

Test castings were cast in moulds from self-setting moulding mixtures. The material for manufacture of moulds was prepared from the base sand  $SiO_2$  bound with phenol-alkaline resin (ALPHASET).

Test castings were Y blocks with a thickness of 60 mm (Y60). From each chemical composition of the metal always one Y60 block was cast. A hand ladle was used for casting. After casting the risers were covered with the EXO powder. For checking the temperature drop during cooling a thermocouple was inserted in each cast block.

Three Y60 test blocks with graduated nickel content and chemical composition given in Table 2 were cast from the experiment.

Table 2  
Chemical composition of cast blocks

Block	331-1	331-2	331-3
Steel	[wt. %]	[wt. %]	[wt. %]
C	0.02	0.02	0.02
Mn	0.76	0.71	0.63
Si	0.41	0.37	0.32
Cr	13.06	12.85	12.68
Mo	0.17	0.17	0.17
Ni	3.55	4.26	5.14
Cu	0.05	0.06	0.06
Al	0.019	0.018	0.015
P	0.008	0.008	0.008
S	0.006	0.005	0.005
N	0.016	0.013	0.013
N <sub>equi.</sub>	5.01	5.61	6.45
Cr <sub>equi.</sub>	13.85	13.58	13.33

It is evident from the concentrations listed in Table 2 that the resulting nickel contents very well cover a range given by the standard and correspond to the planned values of nickel equivalents.

## 2.2. Manufacture of mould and pouring of castings

Four plates of the size 60 × 115 × 24 mm were cut of each block. They were marked with the number 1 to 4 added after the indication referred to in Table 2. Three plates designated (313-1-1, 313-2-1 and 313-3-1) were left in as cast condition. Other plates had holes of a diameter of 3.5 mm drilled into the centre of the plate for inserting a clad thermocouple of the K type. These plates were subsequently subjected to thermal treatment, quenching and tempering.

The heat treatment quenching regime consisted of heating to temperature of 1030 °C with holding for 1 hour and subsequent cooling to ambient temperature by three differently intensive ways:

- in quiet air (samples 313-1-2, 313-2-2 and 313-3-2)
- on flowing air with the aid of a fan (samples 313-1-3, 313-2-3 and 313-3-3)
- on flowing air with water fog (samples 313-1-4, 313-2-4 and 313-3-4)

After quenching the all test plates were commonly tempered under 620 °C for 2 hours with cooling in the furnace. Courses of cooling from the austenitization temperature for individual cooling ways were determined from the thermocouple records. Achieved average cooling rates in the range of 960-600 °C are given in Table 3.

Table 3  
Average rates of cooling the samples

Intensity of cooling	Quiet air	Flowing air	Flowing air with water fog
Cooling rate	98 [°C/min]	117 [°C/min]	124 [°C/min]

## 3. Experimental results

### 3.1. Mechanical properties

Each heat treated plate was divided in 3 longitudinal sections and test samples for the tensile test were made always from the outermost parts (marked A and B). A total 18 test pieces were prepared in such a way.

Values of ultimate tensile strength UTS [MPa], of the yield strength YS [MPa] and elongation E [%] were tested. Table 4 gives values of mechanical properties achieved with values of Ni<sub>equi.</sub> from samples A and B (313-1-2, 313-2-2, 313-3-2) after heat treatment in quiet air, from samples A and B (313-1-3, 313-2-3, 313-3-3) after heat treatment on flowing air with the aid of a fan and from samples A and B (313-1-4, 313-2-4 a 313-3-4) after heat treatment on flowing air with water fog.

Table 4  
Achieved results of chosen mechanical values

Sample No.	Ni <sub>equi.</sub>	YS [MPa]	UTS [MPa]	E [%]	R.A [%]
313-1-2 A	5.01	694	856	12.7	59.5
313-1-2 B	5.01	693	837	13.7	63.7
313-1-3 A	5.01	623	786	16.5	65.1
313-1-3 B	5.01	618	780	16.7	65.9
313-1-4 A	5.01	648	768	18.1	66.8
313-1-4 B	5.01	624	766	18.9	68.3
313-2-2 A	5.61	662	847	13.9	64.4
313-2-2 B	5.61	656	834	14.6	65.4
313-2-3 A	5.61	606	795	15.6	51.4
313-2-3 B	5.61	614	801	16.2	66.3
313-2-4 A	5.61	594	774	19.1	67.3
313-2-4 B	5.61	587	781	17.3	66.1
313-3-2 A	6.45	706	936	12.7	63.1
313-3-2 B	6.45	691	917	13.0	56.9
313-3-3 A	6.45	610	833	16.3	66.7
313-3-3 B	6.45	631	855	14.9	61.8
313-3-4 A	6.45	571	780	19.6	68.5
313-3-4 B	6.45	610	779	20.3	62.4

Individual results have been incorporated into the graphic representation (Figure 1 – Figure 3).

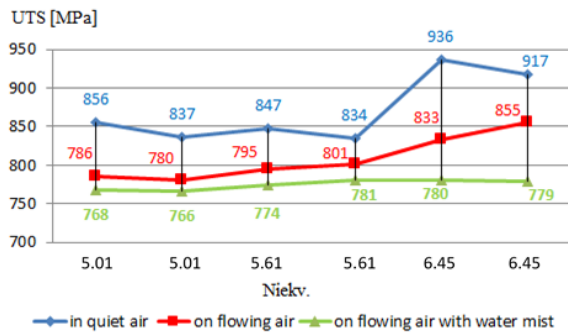


Fig. 1. Achieved values of ultimate tensile strength in dependence on the value of nickel equivalent and the intensity of cooling during quenching

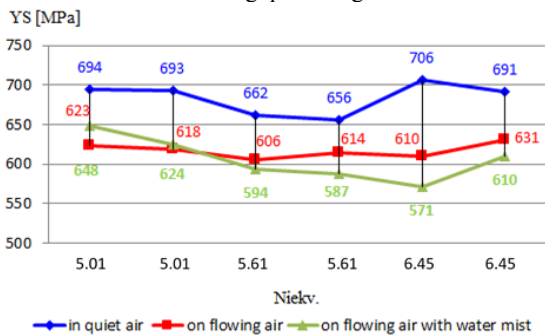


Fig. 2. Achieved values of yield strength in dependence on the value of nickel equivalent and the intensity of cooling during quenching

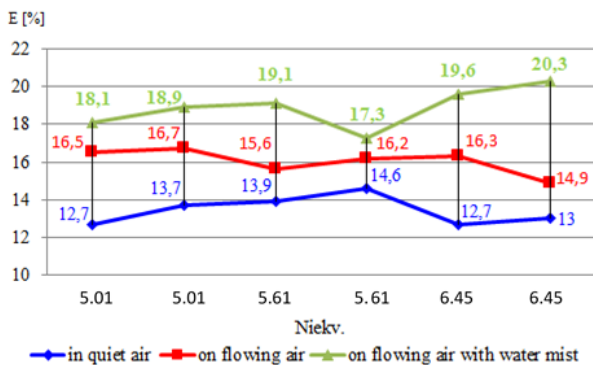


Fig. 3. Achieved elongation values in dependence on the value of nickel equivalent and the intensity of cooling during quenching

It is valid for all graphical representations of individual mechanical values that on the x axis the first two Ni<sub>eqv.</sub> values are after heat treatment in quiet air, the other two Ni<sub>eqv.</sub> values after heat treatment on flowing air with the aid of a fan and the last two Ni<sub>eqv.</sub> values after heat treatment on flowing air with water fog.

### 3.2 Microstructure

Materials of the test blocks were evaluated metallographically in as cast condition and after heat treatment. Metallographic samples were taken from the head part of test bodies for the tensile test after their breaking. Figure 4 shows the microstructure of the material in as cast condition with nickel equivalent value Ni<sub>eqv.</sub> of 5.01 (Ni content 3.55%). Figure 5 shows the microstructure of the same material Ni<sub>eqv.</sub> of 5.01 but after quenching and tempering with cooling the material during quenching in quiet air. Microstructure of the same material with Ni<sub>eqv.</sub> of 5.01 but after quenching on flowing air with the aid of a fan and tempering is shown in Figure 6. Figure 7 also shows the microstructure of the material with Ni<sub>eqv.</sub> of 5.01 but after quenching and tempering with the use for cooling the flowing air and water fog.

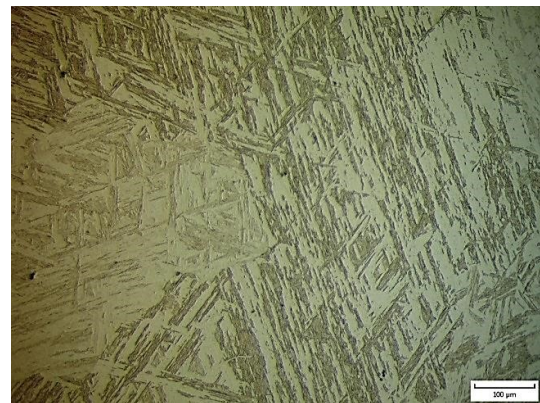


Fig. 4. Microstructure of steel with 5.01 Ni<sub>eqv.</sub> in the as cast condition



Fig. 5. Microstructure of steel with 5.01 Ni<sub>eqv.</sub> after quenching and tempering, quenching in quiet air

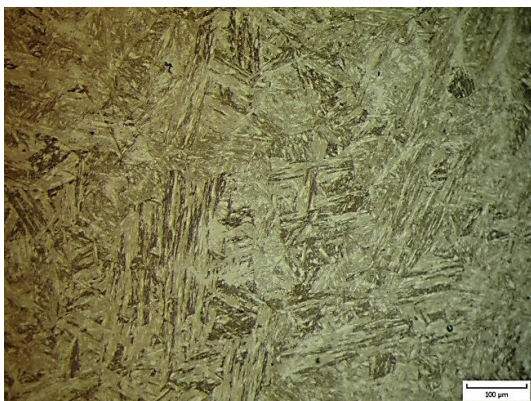


Fig. 6. Microstructure of steel with 5.01 Ni<sub>equi.</sub> after quenching and tempering, quenching on flowing air with the aid of a fan

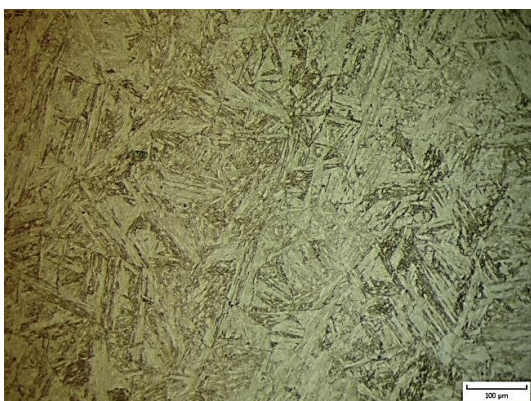


Fig. 7. Microstructure of steel with 5.01 Ni<sub>equi.</sub> after quenching and tempering, quenching with flowing air with water fog

Relatively coarse martensite particles are found in the structure in as cast condition. With slow cooling after quenching and tempering (quiet air) the structure is martensitic one with small particles of ferrite formed on grain boundaries. Using more intensive cooling (flowing air, flowing air + water fog) there is a significant refinement of martensitic laths and the deposition of ferrite on grain boundaries is suppressed. Evaluation of the ferrite volume in structure from metallographic samples after quenching and tempering with the use of more intensive cooling is no longer possible. For determining the phase composition it is necessary to use either the X-ray diffraction analysis or the pattern analysis with the use of measuring the microhardness. It is also possible to take advantage of the knowledge that the ferrite in martensitic steels is significantly enriched with chromium and molybdenum, compared to the surrounding matrix.

## 4. Discussion

Properties of martensitic stainless steel 1.4317 were studied during this research. The results of the experiment showed that the achieved mechanical properties at the tensile test comply with all requirements of the standard. Values of tensile strength and yield point significantly exceeded the requirements of heat

treatment QT1 according to DIN with three different values of nickel equivalent within 5.01 or 5.61 and 6.45. The desired values of ultimate strength and yield point were satisfying in all three ways of heat treatment, on quiet air, on flowing air using a fan and on flowing air with water fog.

Achieved tensile strength values are satisfying and they exceed the values of the material with Ni<sub>equi.</sub> of 5.01; 5.61 and 6.45 during heat treatment, on flowing air using a fan and on flowing air with water fog. The results of the values of the material with Ni<sub>equi.</sub> (5.01; 5.61; 6.45) with heat treatment on quiet air are just below the values prescribed by the standard. It follows from the obtained results that for the required tensile strength values it is necessary to ensure a higher rate of cooling the material during quenching than just on quiet air. An important thing is to achieve a certain cooling rate in the cross section of the material; the question is not the surface temperature of the given sample. The cooling rate values given in Table 3 correspond to values measured in the material in the axis of the wall thickness of 24 mm.

As it is apparent from Figure 4 up to Figure 7 with increasing intensity of cooling during quenching the martensite laths are significantly refined and the deposition of ferrite particles on grain boundaries is suppressed.

Properties of martensitic stainless steels with a nickel equivalent value of around 5.40 will be studied in further research.

## 5. Conclusions

An influence of the nickel equivalent value and the intensity of cooling during quenching on properties of the martensitic stainless cast steel GX4CrNi13-4 has been proved. Structure of steels was studied in the as cast condition and after heat treatment, mechanical properties after quenching and tempering only. By changing the nickel content with otherwise constant composition the value of the nickel equivalent was changed within 5.01 or 5.61 and 6.45.

Due to evaluating the mechanical properties in tensile test it has been confirmed that the satisfactory values of mechanical properties are achieved regardless of the value of the nickel equivalent only if a higher intensity of cooling the steel during quenching is applied. The treatment of the steel on quiet air did not lead in any of the tested materials to the achievement of the desired elongation to fracture.

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