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Structure and properties of Super 304H steel for pressure elements of boilers with ultra-supercritical parameters

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Properties

ABSTRACT

Purpose: Material condition assessment with regard to required utility properties of Super304H austenitic steel for operation at elevated temperature.

Design/methodology/approach: The structural and mechanical testing at room and elevated temperature after annealing at 650°C and 700°C for 1000 and 3000 h was carried out.

Findings: The effect of temperature and duration of long-term annealing on mechanical properties, hardness and structure of tested was determined.

Practical implications: The presented method can be used for evaluation and qualification of structural changes in power station boiler components operating in creep conditions.

Originality/value: The presented results of changes in the mechanical properties, structure and in the precipitation processes are applied to evaluation the condition of the elements in further industrial service.

Keywords: Structure; Hardness; Creep; Steel Super 304H

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1. Introduction

Since at least the end of the 1990s, the increased works and numerous research programmes aiming at maintenance of the current level of heat and electric power production have been conducted in Poland [1-10, 15-17]. The result of these works is not only the reliable diagnostics and renovation of power units operated for a long time and whose work time has already exceeded the assumed design time a long time ago, but also the construction of new units with supercritical steam parameters, i.e. temperature of 600ºC and pressure of 25-30 MPa.

However, the worldwide aspirations for ensuring energy safety with simultaneous tightening of the requirements of the act on permissible emission of pollutants into the atmosphere have contributed to the development of materials that allow the improvement of steam working parameters resulting in units designed for ultra-supercritical steam parameters.

The construction of boilers with ultra-supercritical steam parameters between 550 and 760°C requires the use of new materials with higher and higher mechanical parameters and more and more complex manufacturing process for making the components of boiler pressure section out of them [3]. Among the critical boiler pressure section components, there should be distinguished, among other things, the thin-wall pipes of steam superheaters whose materials can be operated at up to approx. 600°C and 25-30 MPa in systems with supercritical parameters. The materials more and more often used for components of steam superheater with so high parameters are nonferrous alloys, mainly based on nickel, as well as high-temperature corrosion resistant steels of austenitic structure, which include, but are not limited to, Super304H steel developed in the 1990s. This steel is characterised by high heat resistance, and the addition of copper in the amount of approx. 3% wt significantly improved its creep strength.

For materials that boiler components are made out of the characteristics are developed to acquire knowledge on their behaviour under the operating conditions. Due to the specific operating nature of the materials, the construction of these characteristics and revealing of degradation and destruction processes that occur in them is a long-term operation and covers approx. 15 to 20 years.

This paper presents the results of investigations on material of finished component which is the steam superheater coil made of Super304H steel. The creep strength was determined and mechanical testing was carried out. The structure of material and its fitness for manufacture of boiler pressure section components for ultra-supercritical parameters with regard to the requirements placed on them were assessed.

2. Research material

The research material was a section of steam superheater coil pipe made of Super304H steel with dimensions of ø 42.4 x 8.8 mm. Chemical composition of the steel tested with regard to the requirements of standard is presented in Table 1.

3. Research scope

As a part of the tests, the properties of tested material were determined. In the assessment of material condition and level of required utility properties of tested steel for service at elevated temperature, the determination of creep strength in the abridged creep tests and determination of the effect of temperature and duration of long-term annealing on mechanical properties and structure of tested material were assumed to be particularly important.

The selected investigation results obtained so far and the assessment of properties of austenitic Super304H steel are presented below.

4. Research results

4.1. Influence of long-term annealing on mechanical properties of tested steel

The obtained test results of tensile strength TS, yield point YP, elongation and reduction of area in static tensile test at room temperature and within the temperature range between 450 and 650ºC for tested steel in initial state are presented in Fig. 1, while the change in these properties after annealing at 650 and 700°C for 1000 and 3000 h is presented in Figs. 2 and 3, respectively. The results of impact energy KV at a temperature between -60 and +20°C for material in initial state are presented in Fig. 4, while changes in the values of impact energy after annealing at 650 and 700°C for 1000 and 3000 h are presented in Fig. 5.

The results obtained in static tensile test at room and elevated temperature for Super304H steel in initial state and after annealing at 650 and 700°C for 1000 and 3000 h comply with the requirements of ASME Code Case 2328-1 [11], whereas after annealing at both 650°C and 700°C for 1000 and 3000 h it was observed that the yield point YP at both room temperature and elevated temperature, similar to the expected working temperature, increased in relation to that in initial state.

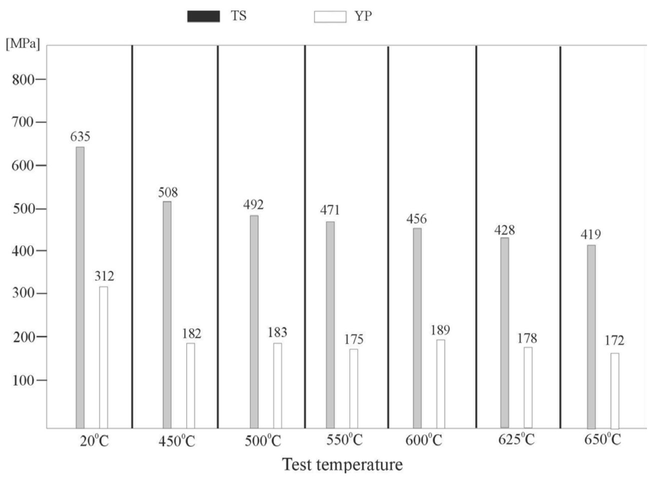

Fig. 1a. Values of tensile strength and yield point of tested steel in initial state

Table 1.
Chemical composition of material of tested pipe made of steel Super 304H

	Chemical composition [%]											
	C	Si	Mn	P	S	Cu	Cr	Ni	Nb	B	N	Al
Check analysis	0.09	0.20	0.80	0.0032	0.000	2.99	18.4	8.8	0.48	0.004	0.11	0.0006
ASME Code Case 2328-1	0.07 0.13	max 0.30	max 1.00	max 0.0040	max 0.0010	2.50 3.50	17.0 19.0	7.5 10.5	0.30 0.60	0.0001 0.0010	0.05 0.12	0.0003 0.0030

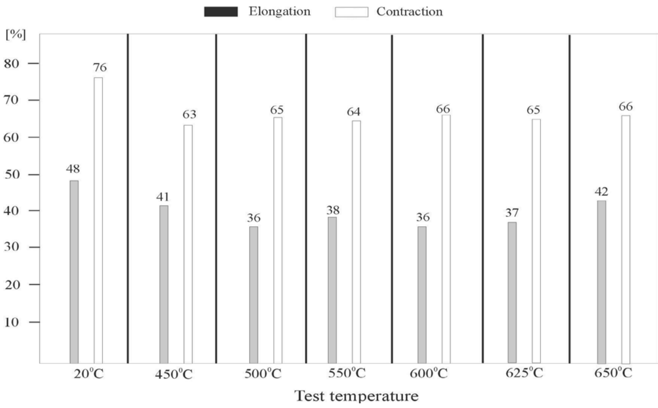

Fig. 1b. Values of elongation and reduction of area of tested steel in initial state

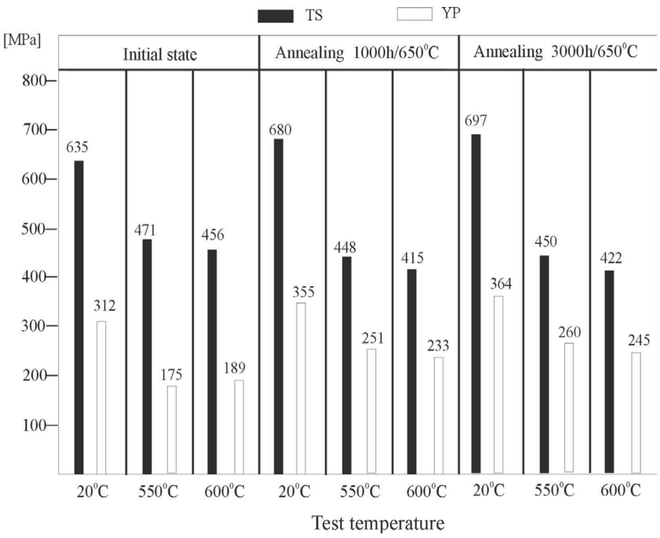

Fig. 2a. Values of tensile strength and yield point after annealing at 650°C for 1000 and 3000 h

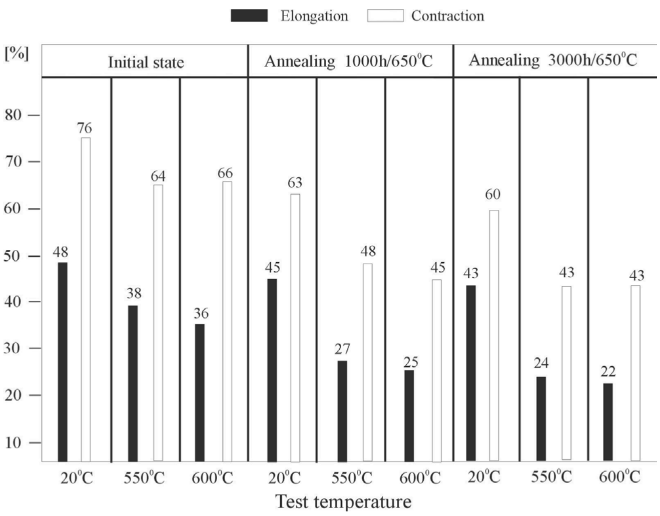

Fig. 2b. Values of elongation and reduction of area after annealing at 650°C for 1000 and 3000 h

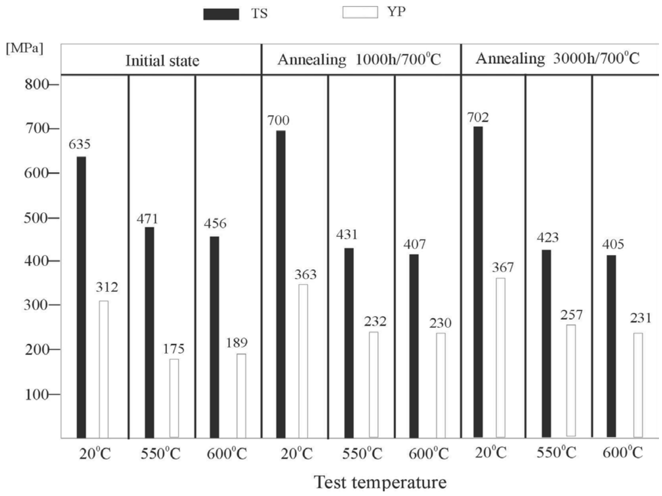

Fig. 3a. Values of tensile strength and yield point after annealing at 700°C for 1000 and 3000 h

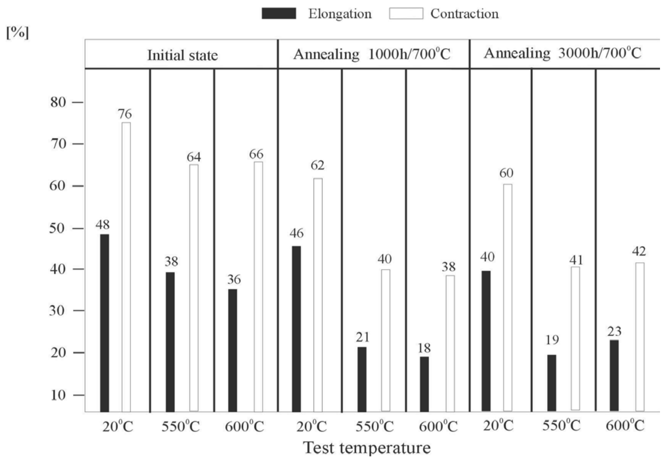

Fig. 3b. Values of elongation and reduction of area after annealing at 700°C for 1000 and 3000 h

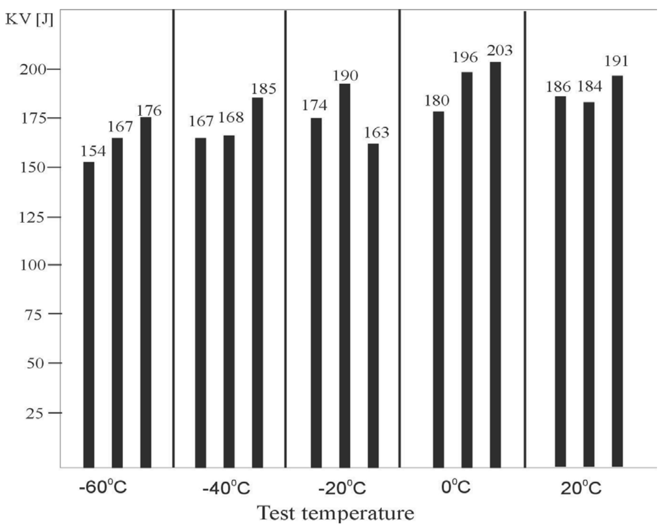

Fig. 4. Impact energy of tested steel in initial state

However, the reduction in plastic properties, whose values after annealing for 1000 and 3000 h are on similar level, was observed. The obtained values of impact energy at room temperature fell from approx. 185J to approx. 85J after annealing for 1000 and 3000 h.

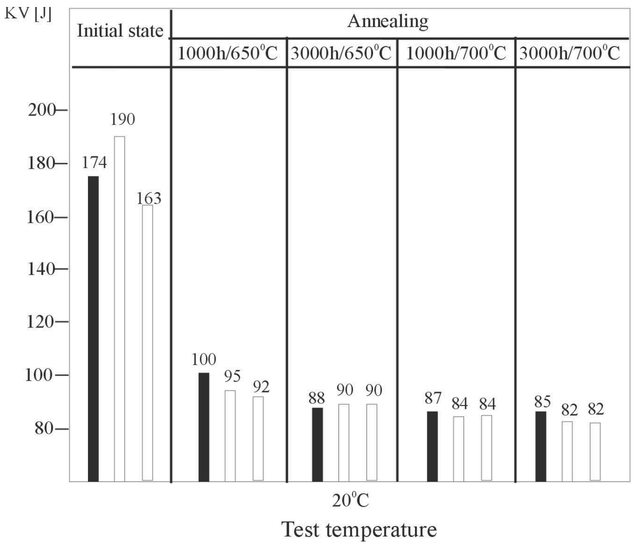

Fig. 5. Impact energy of tested steel after annealing at 700°C for 1000 and 3000 h.

4.2. Assessment of life time in abridged creep tests

The disadvantage of the method for determination of life time using long-term creep tests is the time of waiting for test results, which is at least 2 to 5 years. In order to reduce the duration of these investigations and life time assessment, in the engineering practice the so-called abridged creep tests lasting from a few dozen hours to max 3 to 10 thousand hours are used. It creates the opportunity to obtain test results within max several months, providing good estimation of the life time. The acceleration of the creep process and reduction in testing period is obtained for creep tests carried out at uniaxial tension on test pieces taken from the material of power system component by conducting tests: - at constant test stress equal to the service one and different levels of test temperature, much higher than the service temperature, and at constant test temperature equal to the service one and different levels of test stress, higher than the service stresses. The results of the abridged creep tests conducted at a constant stress equal to the service one and in long-term creep tests as a part of own investigations carried out at the Institute for Ferrous Metallurgy verified the method positively, which allowed its use in the engineering practice for steels used so far for critical components of the pressure part of boilers. Fig. 6 presents the graphic method for determination of life time using the abridged creep tests.

Creep tests without measurement of elongation during the test were carried out using multi-sample machines for creep tests manufactured by the Institute for Ferrous Metallurgy. The machines are equipped with load applying systems located in the heating chambers with constant temperature to provide stable test temperature level over the gauge length of a test piece and during the test, with accuracy of 1 degree at test temperature of up to 800°C. The tests were performed on standard test pieces with ratio $l_0/d_0 = 5$, gauge length $l_0 = 25$ mm and gauge diameter of test piece $d_0 = 5$ mm, sampled along the pipe axis.

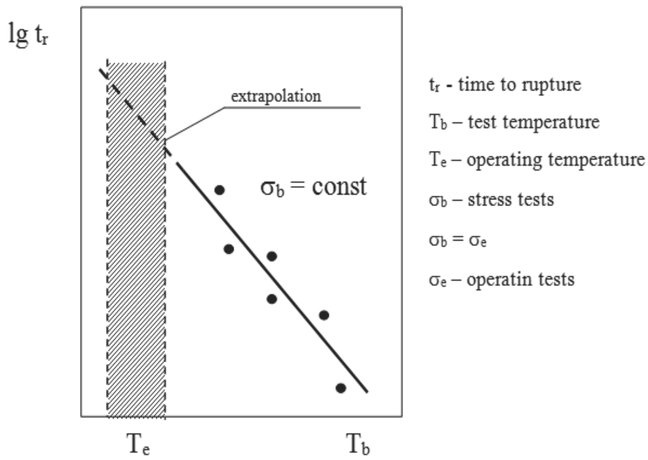

Fig. 6. Method for determination of life time based on abridged creep tests

The results of abridged creep tests are summarised in Table 2 and presented graphically in Figs. 7 and 8 as the relationship $\log t_r = f(T_b)$, at test stress σ_b = 150 and 180 MPa, respectively. The results of uncompleted tests are in brackets. Table 3 summarises the forecast life time of tested steel for the expected operating temperature depending on the assumed operating stress σ_b.

Table 2.
Results of abridged creep tests of Super 304H steel

Test stress σ_b [MPa]	Test temperature T_b [°C]				
	650	675	700	725	750
	Time to rupture t_z [h]				
150	(10000)	8330	2050	484	111
180	6770	1805	430	103	22

Table 3.
Forecast life time for tested Super 304H steel based on abridged creep tests

Assumed operating stress σ_r [MPa]	Assumed temperature of further operation T_r [ºC]	Estimated residual life [h]
150	600	600 000
	610	350 000
	620	200 000
180	600	150 000
	610	90 000
	620	50 000

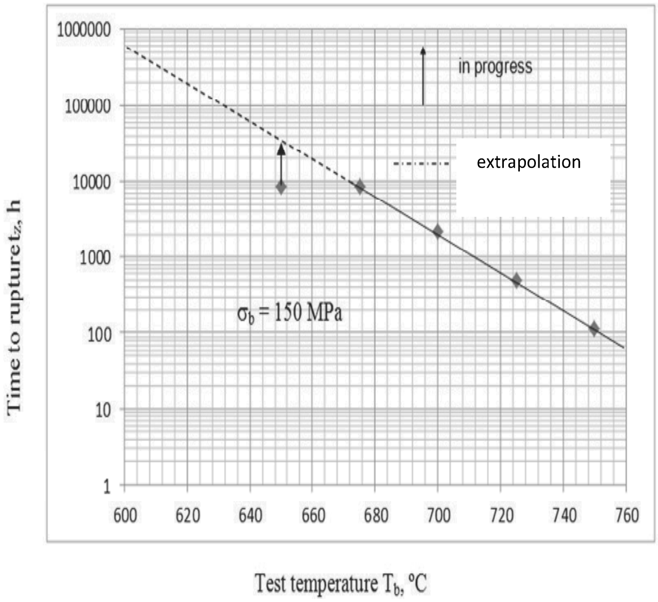

Fig. 7. Results of abridged creep tests presented as the relationship $\log t_z = f(T_b)$ for Super 304H steel at σ_b=150 MPa

The obtained results of abridged creep tests allowed the life time of tested Super 304H steel to be estimated. Thus, it can be stated that the tested material of sections in the form of steam superheater coils meets the requirements of creep strength in relation to literature data [11]. The results obtained in abridged creep tests coincide with creep strength according to Code Case 2328-1.

4.3. Influence of long-term annealing on structure of Super 304H steel

The long-term impact of temperature on the material structure is controlled by thermally activated processes. As the temperature rises, these processes are accelerated and at the same time they reduce the set of utility properties of the material and the component made of it. Microstructure of austenitic steels is subject to changes consisting in decay and/or growth of initial structural components and precipitation processes the course of which is the competing dissolution and secondary precipitation processes [12-14]. The evaluation of these changes with reference to the level of utility properties is one of the elements to be achieved as a result of the structural investigations on test pieces after long-term annealing. The structural investigations were performed using scanning electron microscope.

Long-term annealing of Super 304H austenitic steel is conducted at two temperature levels, i.e. 650 and 700°C. The investigations of mechanical properties, hardness, structural condition and development degree of precipitation processes were performed for initial state as well as after 1000 and 3000 hours. Tests after 5000, 10000 and 20000 hours of long-term annealing at the above-mentioned temperature levels are also conducted and they will be the subject of future publications.

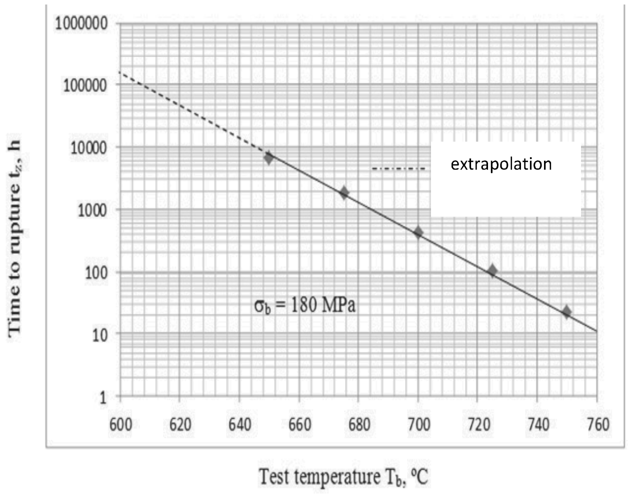

Fig. 8. Results of abridged creep tests presented as the relationship $\log t_z = f(T_b)$ for Super 304H steel at σ_b=180 MPa

The steam superheater pipe made of Super 304H steel in initial state, which was selected for testing, is characterised by austenitic structure with few precipitations within the grains and at grain boundaries and by Nb (C,N) niobium carbonitride precipitations (Fig. 9). The annealing at 650°C for 1000 and 3000 h resulted in the increase in size of Nb (C,N) niobium carbonitride precipitations and very fine $Cr_{23}C_6$ carbide precipitations at austenite grain boundaries (Figs. 10, 11). No significant differences in structure image after annealing at 650°C for 1000 and 3000 h were observed.

The structure image of Super 304H steel after annealing at 700°C for 1000 and 3000 hours (Figs. 12, 13) does not differ significantly from that observed after annealing at 650°C. The observed structure is austenite with Nb(C,N) carbonitride precipitations both within the grains and at grain boundaries and $Cr_{23}C_6$ carbide precipitations at grain boundaries, which form precipitation chains in places (Fig. 13).

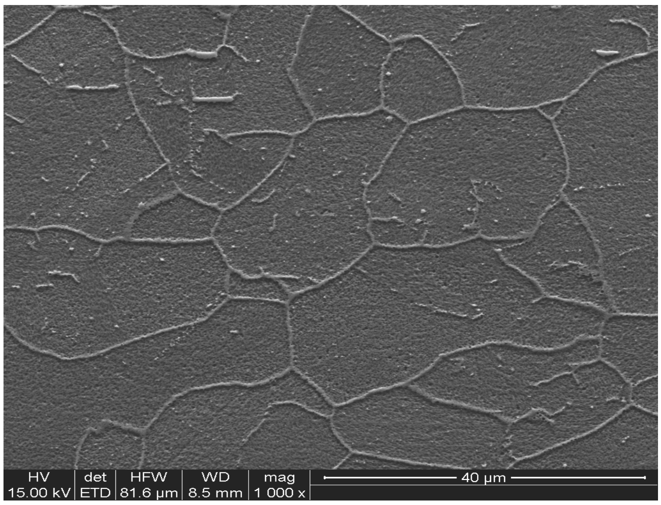

Fig. 9. Structure of Super 304H steel in initial state, observed using scanning electron microscope (hardness 198 HV10)

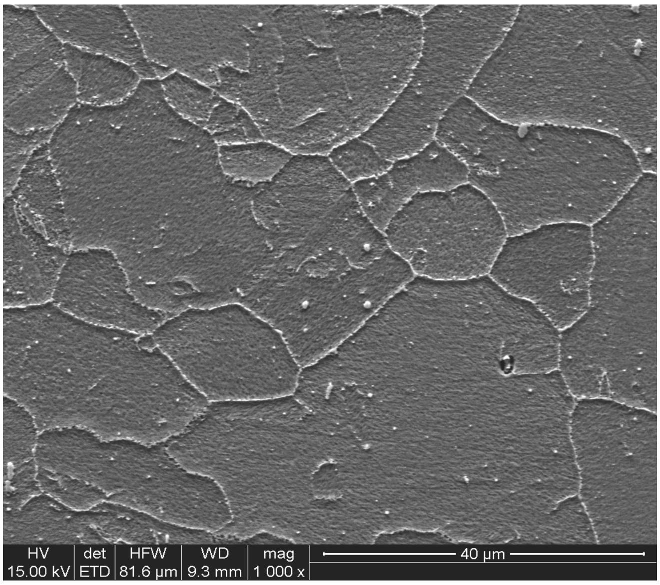

Fig. 10. Structure of Super 304H steel after annealing at 650°C for 1000h, observed using scanning electron microscope (hardness 220 HV10)

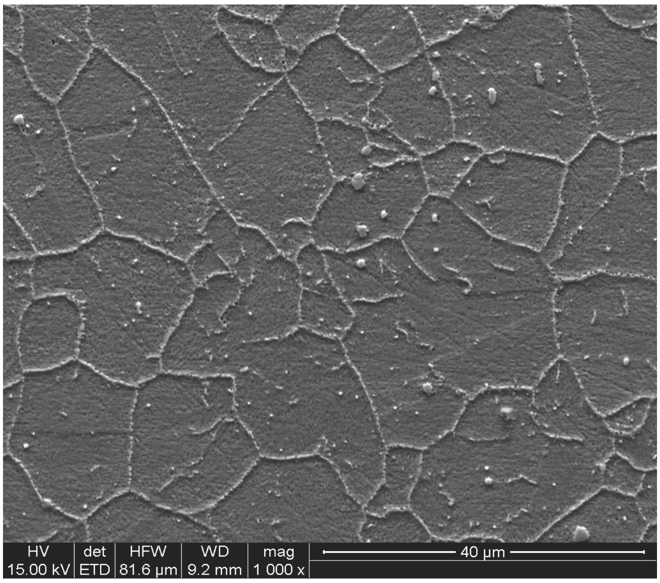

Fig. 11. Structure of Super 304H steel after annealing at 650°C for 3000h, observed using scanning electron microscope (hardness 232 HV10)

To identify the distribution of alloying elements and their contents in precipitations within the structure of Super304 H steel after long-term annealing at 700°C for 3000h, the chemical composition microanalysis was performed. The test results are presented in Fig. 14. Based on the analysis, the concentration of niobium, carbon and nitrogen is visible where Nb (C,N) carbonitride is observed in the micro-area. The increased amount of chromium and carbon was also observed at austenite grain boundaries where $Cr_{23}C_6$ carbides are precipitated as a result of long-term annealing.

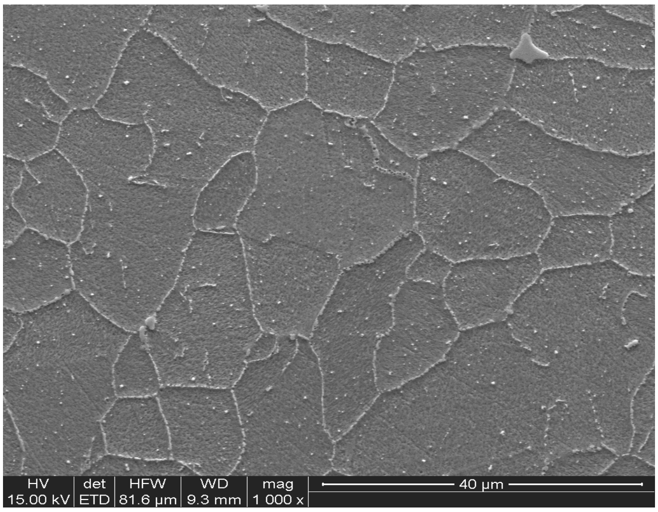

Fig. 12. Structure of Super 304H steel after annealing at 700°C for 1000h, observed using scanning electron microscope (hardness 199 HV10)

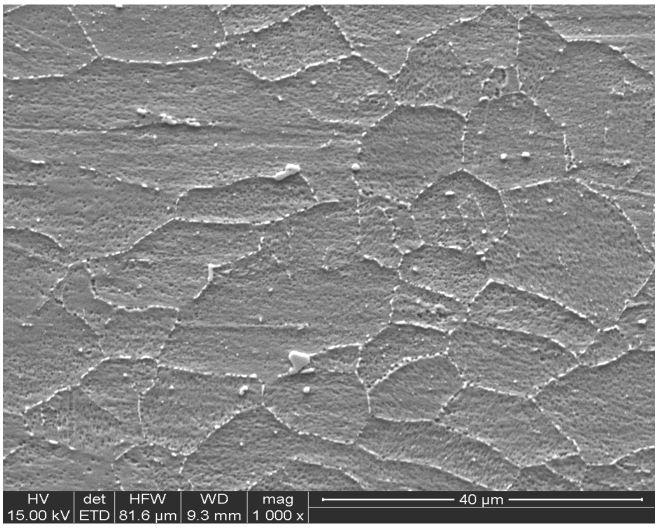

Fig. 13. Structure of Super 304H steel after annealing at 700°C for 1000h, observed using scanning electron microscope (hardness 205 HV10)

5. Conclusions

The investigations carried out on Super 304H austenitic steel allow finding out that:

- The material of tested coil in initial state made of Super 304H steel meets the requirements for basic mechanical properties at room temperature and at the temperature of expected operation.
- Impact energy for material in initial state measured within the temperature range between -60°C and 20°C is much higher than the minimum requirements placed on this steel.
- Annealing at 650 and 700°C for 1000 and 3000 h resulted in increase in yield point both at room and elevated temperature.

However, it caused a decrease in plastic properties of elongation and reduction of area. Significant decrease in impact energy to approx. 80J was also observed.

- The abridged creep tests performed at constant stress level of σ_b = 150 and 180 MPa and at a temperature higher than the assumed working temperature allowed the life time evaluation of the material of tested steam superheater coil. The determined creep strength is in compliance with Code Case 2328-1.
- In the microstructure of tested steel after long-term annealing at 650 and 700°C for up to 3000 hours, the austenite structure with Nb(C,N) carbonitride precipitations both within the grains and at grain boundaries and $Cr_{23}C_6$ carbide precipitations at grain boundaries, which form precipitation chains in places, was observed.

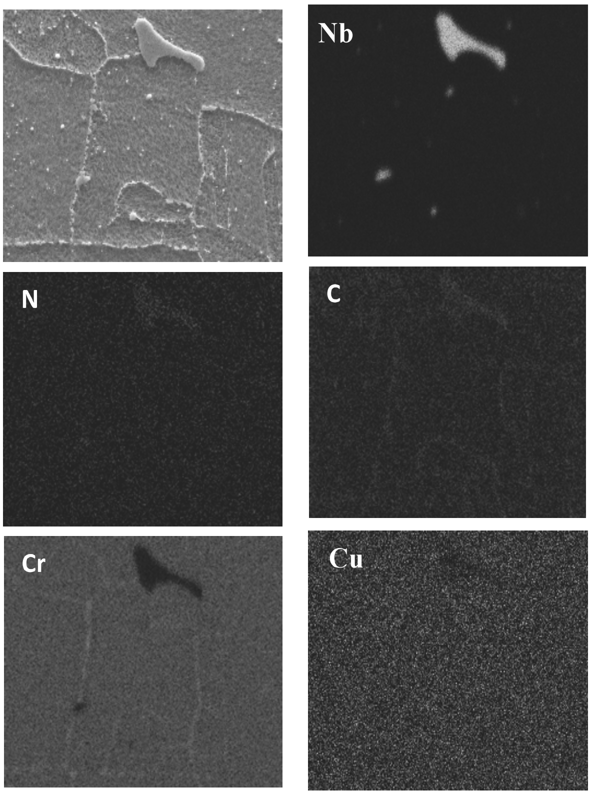

Fig. 14. Chemical composition microanalysis of elements within the structure of Super304H steel after annealing at 700°C for 3000 h

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