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Austenitic steels for boiler elements in USC power plants

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Materials

ABSTRACT

Purpose: Characteristics of functional properties of austenitic-based steels used for construction of boilers with supercritical and ultra-supercritical steam parameters.

Design/methodology/approach: For selected austenitic steels in as-received state and after long-term annealing microstructural investigations were carried out with scanning and transmission electron microscope.

Findings: Selected characteristics of structure and functional properties of materials to be used for critical elements in the pressure section of power boilers were summarised in a single paper

Practical implications: The steel characteristics presented in this paper are used for assessment of structural changes and changes in strength properties of material of elements after long-term service under creep conditions.

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

Keywords: Structure; Creep; HR3C steel; Super 304H steel

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1. Introduction

The world power system is based on thermal power engineering in 60%, and fossil fuels will still be the main raw material used for production of electric energy. According to the literature data, deposits of coal which are sufficient to maintain the current state in energy production can be exploited for at least 100 years to come [1]. Therefore, the care of energy safety, economic use of fossil fuels and need to meet more and more stringent ecological requirements of the European Union force to take effective investment actions, aimed at improving the efficiency of power units, which in turn is conditioned by the development of new materials [2-12]. At present, austenitic steels and nickel superalloys are used for construction of boilers with supercritical steam parameters, i.e. temperature 565-620°C and pressure up to 30 MPa, and ultimately ultra-supercritical parameters, i.e. 650-720°C and 30-35 MPa, and the investigations of functional properties and development of this group of materials has become the key factor in design and construction of new power units [13-16]. It needs to be emphasised that this group of steels and alloys is used for critical elements, which include, but are not limited to, coils in final stages of primary and secondary steam superheaters.

As compared to ferritic-based steels, austenitic steels for service at elevated temperature are characterised by better high-temperature creep and heat resistance and are used for boiler elements working at above 600°C.

The first attempts to use austenitic steels in construction of supercritical boilers were made in the 1960s in USA. The basic austenitic steels and technologies used then did not meet the quality requirements, which resulted in great operating problems and low capacity of these units.

The design work time of newly designed power units is 200-250 thousand hours so the materials used for critical elements of boiler must be reliable at high temperature and pressure for a very long time. The above conditions can only be kept by the use of new-generation austenitic steels and nickel superalloys.

The prototype of austenitic steel for critical elements of power boilers was 18%Cr-9%Ni steel, which has contributed to development of new grades of steel with significantly higher functional properties by being enriched with alloying elements.

Fig. 1 presents the development of austenitic steels for construction of power units. Depending on nature of their impact on steel properties, the additives of alloying element present in these steels can be divided into six basic groups [17]:

- Fe, Ni, Cr - forming solid solution,
- C, N - interstitial, reinforcing the matrix and forming secondary phases,
- Mo, W, V, Co - strengthening solid solution,
- Ti, Nb, Ta, Zr - stabilising (bonding carbon and nitrogen),
- B, Zr – increasing second-phase dispersions and modifying precipitation processes at grain boundaries,
- Ni3(Ti, Al) - γ' providing strengthening with intermetallic phase.

Chemical composition of new-generation materials for use in boiler elements with super- and ultra-supercritical steam parameters are presented in Table 1.

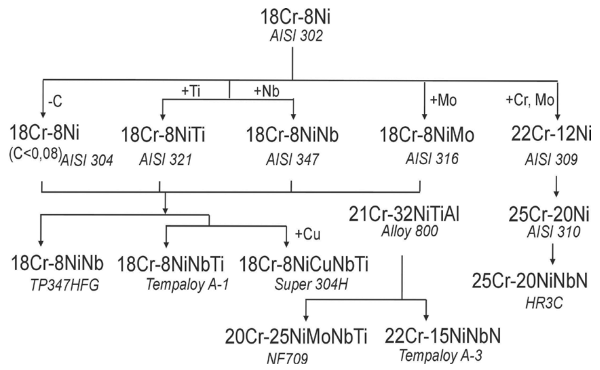

Fig. 1. Development of austenitic steels used in power units [18]

2. HR3C steel

HR3C steel was developed to improve corrosion resistance and oxidation at relatively high strength properties. It is mainly used for elements of steam superheaters. Fig. 2 presents creep-rupture strength of HR3C steel, while Fig. 3 illustrates the comparison of creep-rupture strength of HR3C steel to that of the basic austenitic steels used for steam superheater coils. The characteristic values of creep strength after 10, 30, 100 thousand hours of service within the temperature range of 600-800°C are summarised in Table 2.

In HR3C steel, the main phases are NbCrN, $M_{23}C_6$, MX, δ and Cr_2N. The content of NbCrN and δ phases increases with increase in Nb additive. In HR3C steel, inside grains there are mainly NbCrN and MX phases, while at grain boundaries and partially inside grains - $M_{23}C_6$ precipitations. The existence of brittle δ phase, which results in deterioration of mechanical properties, was observed too [22].

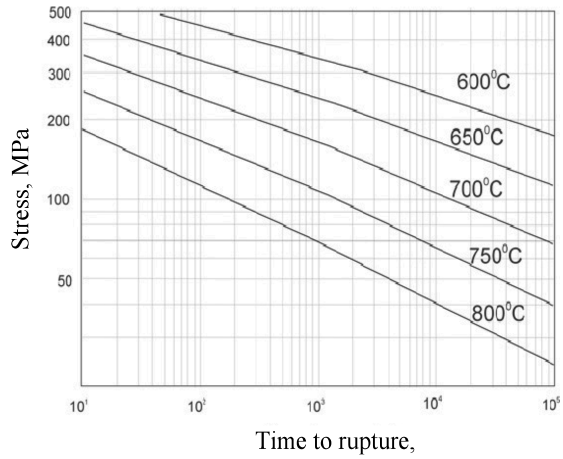

Fig. 2. Creep strength of HR3C steel [19]

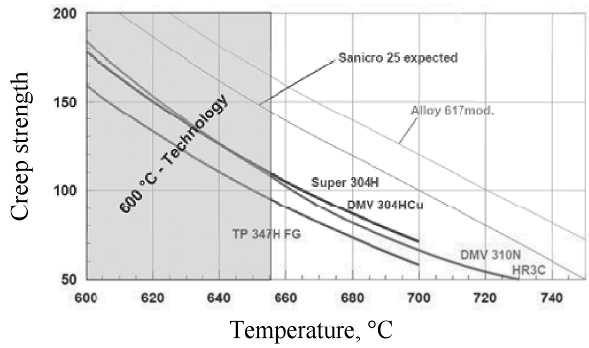

Fig. 3. Creep-rupture strength of HR3C steel as compared to that of the basic austenitic steels used for steam superheater coils [20]

The characteristic image of HR3C steel structure in initial state observed with scanning electron microscope is shown in Fig. 4 and microstructure with identification of NbCrN phase observed with transmission electron microscope - in Fig. 5.

To identify the distribution of alloying elements and their contents in composition of precipitations within the structure of HR3C steel in initial state, the chemical composition microanalysis was performed. The test results are presented in Fig. 6. Based on the analysis, the concentration of niobium, carbon and nitrogen is visible where Nb(C,N) carbonitrides are observed in the micro-area.

3. Super 304H steel

Super304H steel belongs to the group of 18%Cr-9%Ni steels with addition of copper (Cu), niobium (Nb) and nitrogen (N). Like HR3C steel, it is mainly used for elements of steam superheaters. Fig. 7 presents creep-rupture strength of Super 304H steel for the temperature range of 600-700°C. As shown in Fig. 3, creep-rupture strength of Super 304H steel is similar to creep strength of HR3C steel, running at the level of 110 MPa for temperature of 650°C and time of 100,000 h. The characteristic values of creep strength after 10, 30, 100 thousand hours of service within the temperature range of 600-700°C are summarised in Table 3.

Table 1.
Chemical composition of selected steels for use in construction of power boiler

Grade	Chemical composition [%]													
	C	Si	Mn	P	S	Cu	Cr	Ni	W	Nb	B	N	Ti	Al
Super 304H	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
HR3C	0.04 0.10	max 0.75	max 2.00	max 0.03	max 0.03	-	24.0 26.0	17.0 23.0	-	0.20 0.60	-	0.15 0.35	-	-

Table 2.
Creep strength of HR3C steel [19]

Creep strength	Temperature, °C				
	600	650	700	750	800
Rz/10000	266	167	105	67	41
Rz/30000	223	135	84	52	32
Rz/100000	179	107	65	40	25

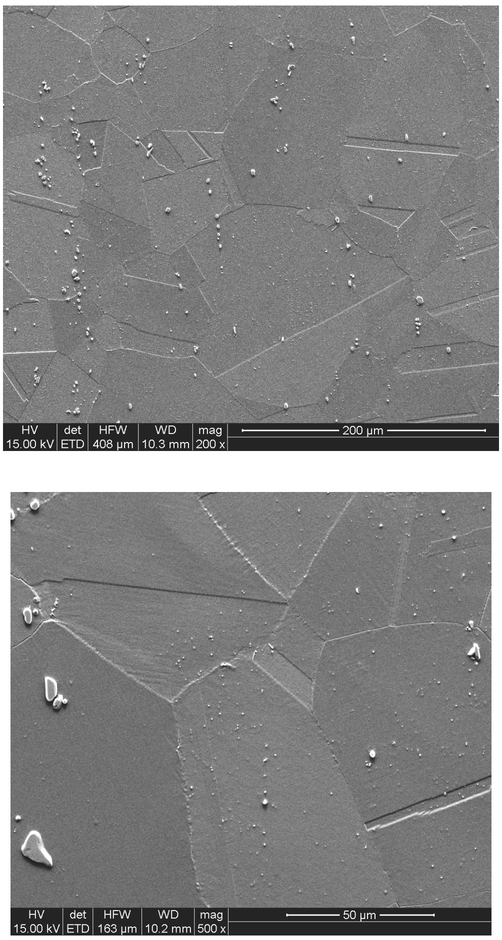

Fig. 4. Microstructure of HR3C steel in initial state observed with scanning electron microscope, hardness 194 HV10

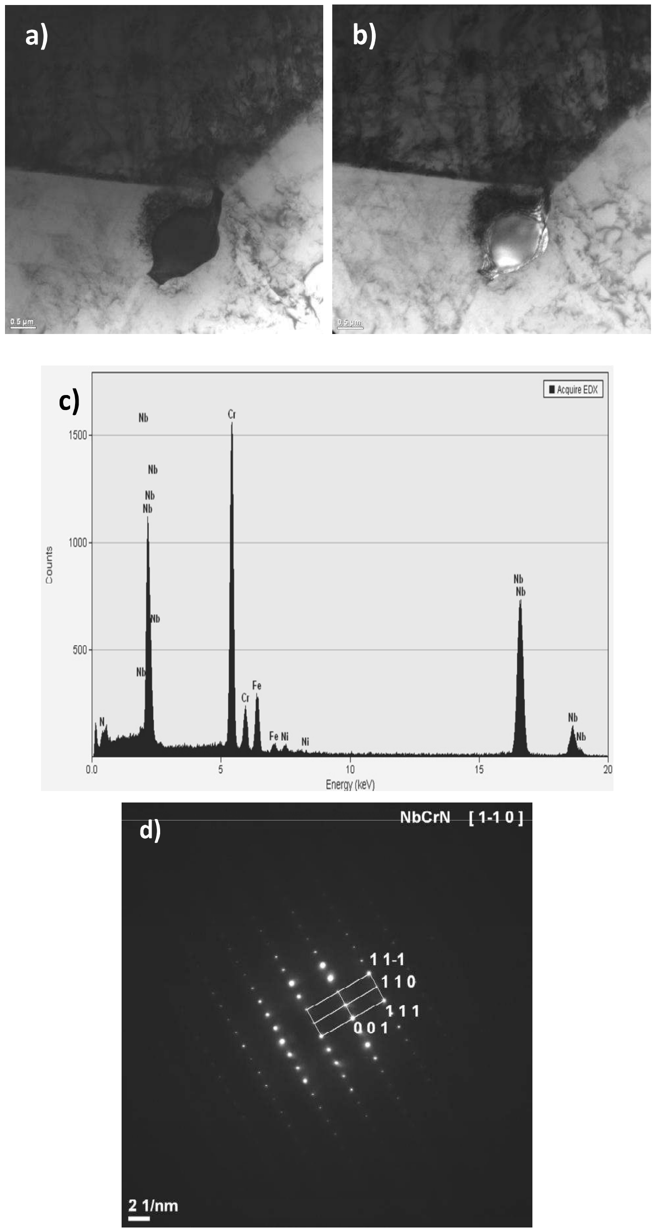

Fig. 5. Microstructure of HR3C steel in initial state observed with TEM a) bright field, b) dark field, c) EDS spectrum for NbCrN phase, d) diffractogram of NbCrN phase

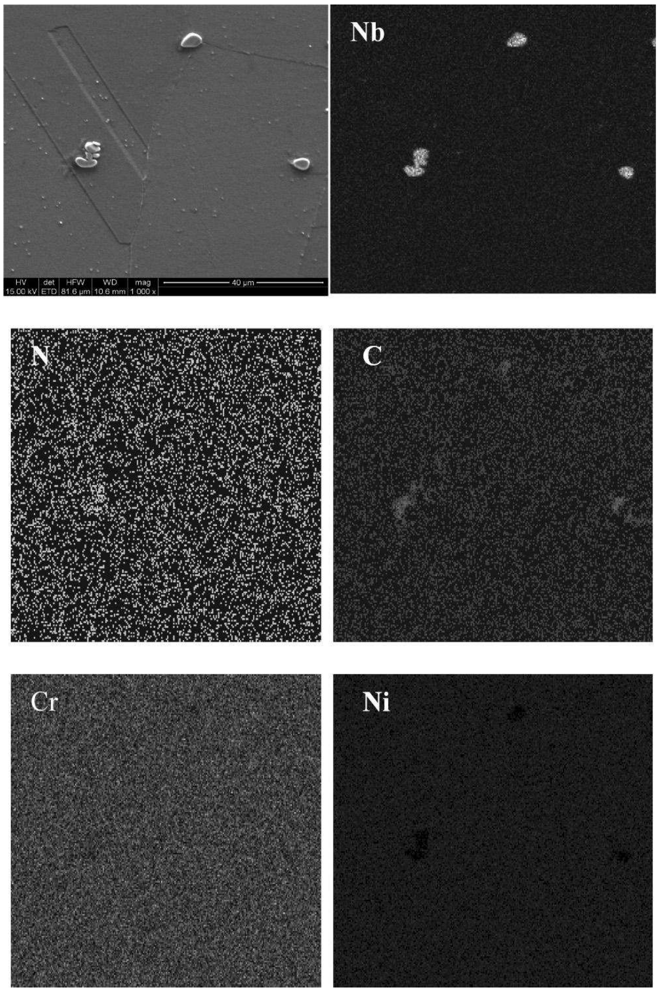

Fig. 6. Chemical composition microanalysis of elements in structure of HR3C steel in initial state

Table 3.
Creep strength of Super 304H steel [21]

Creep strength	Temperature, °C			
	600	650	700	750
Rz/10000	239	165	106	62
Rz/30000	220	140	88	47
Rz/100000	184	120	70	33

The annealing at 650°C for 1000, 3000 and 5000 h resulted in slight increase in the size of Nb (C,N) niobium carbonitride precipitations and very fine $Cr_{23}C_6$ carbide precipitations at austenite grain boundaries (Figs. 9, 10, 11). No significant differences in structure image after annealing at 650°C for 1000, 3000 and 5000h were observed.

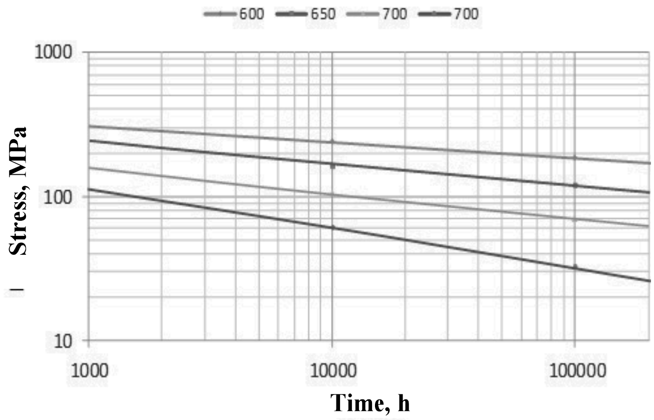

Fig. 7. Creep strength of Super 304H steel [21]

In initial state, Super 304H steel is characterised by austenitic structure with few Nb (C,N) niobium carbonitride precipitations (Fig. 8).

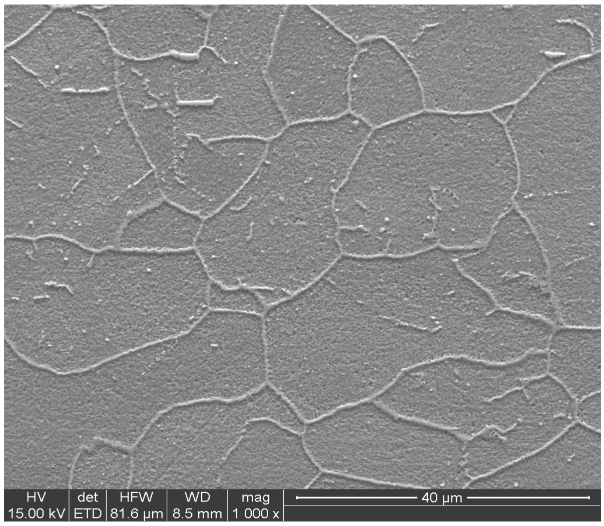

Fig. 8. Structure of Super 304H steel in initial state, observed with scanning electron microscope (hardness 198 HV10)

The structure image of Super 304H steel after annealing at 700°C for 1000, 3000 and 5000 hours (Figs. 12, 13, 14) does not differ significantly from structure image 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. 14).

The identification of precipitations in Super 304H steel in initial state and after long-term annealing was made using transmission electron microscope. The images of microstructure illustrating the type of identified precipitations (M(C,N), NbN) in structure of material in initial state are shown in Fig. 15, while Figs. 16, 17, 18 present the results of microstructure investigations of tested steel after annealing at 700°C for 3000 hours with identified $M_{23}C6$ precipitations, NbCrN and phase rich in copper.

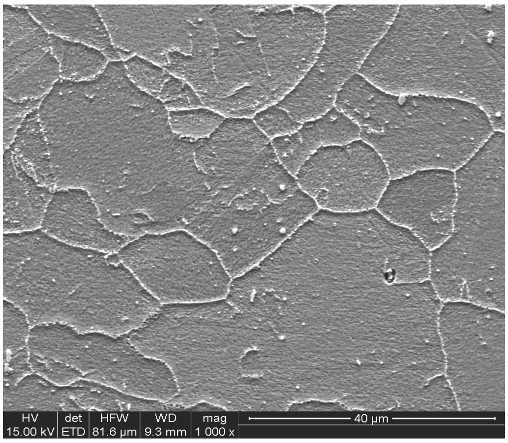

Fig. 9. Structure of Super 304H steel after annealing at 650°C for 1000 h, observed with scanning electron microscope (hardness 220 HV10)

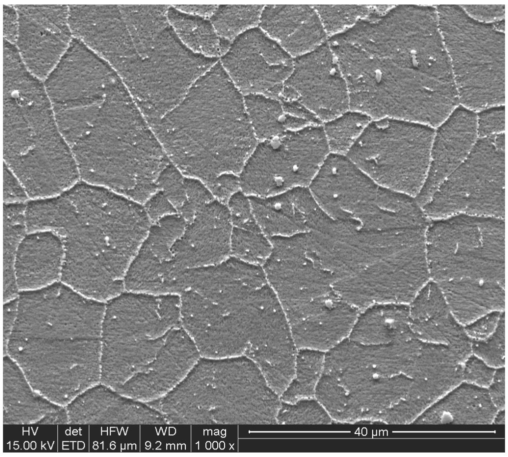

Fig. 10. Structure of Super 304H steel after annealing at 650°C for 3000 h, observed with scanning electron microscope (hardness 232 HV10)

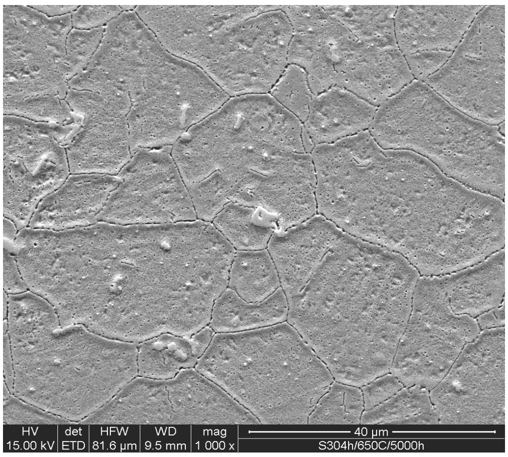

Fig. 11. Structure of Super 304H steel after annealing at 650°C for 5000 h, observed with scanning electron microscope (hardness 207 HV10)

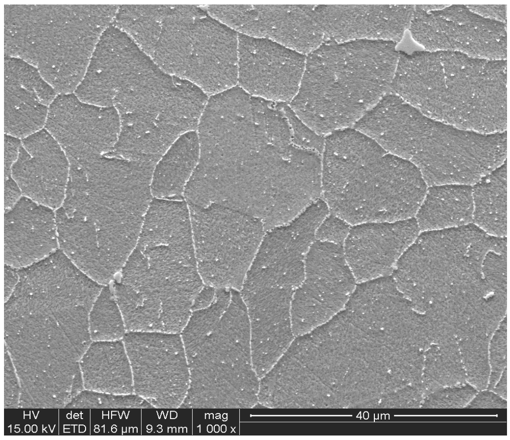

Fig. 12. Structure of Super 304H steel after annealing at 700°C for 1000 h, observed with scanning electron microscope (hardness 199 HV10)

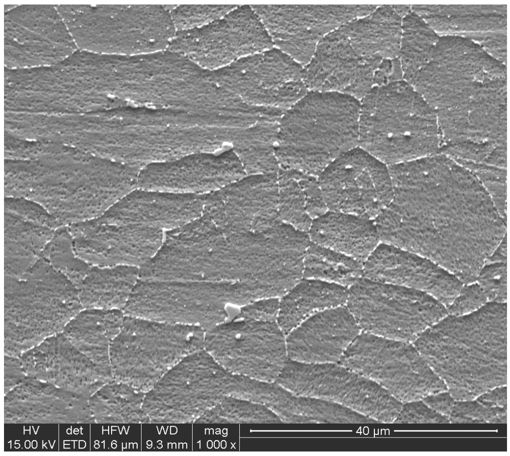

Fig. 13. Structure of Super 304H steel after annealing at 700°C for 3000 h, observed with scanning electron microscope (hardness 205 HV10).

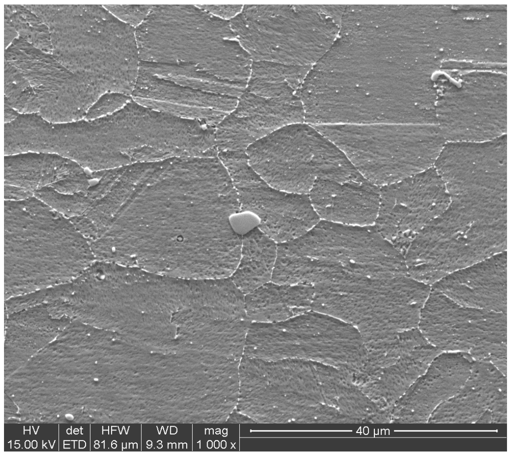

Fig. 14. Structure of Super 304H steel after annealing at 700°C for 5000 h, observed with scanning electron microscope (hardness 196 HV10)

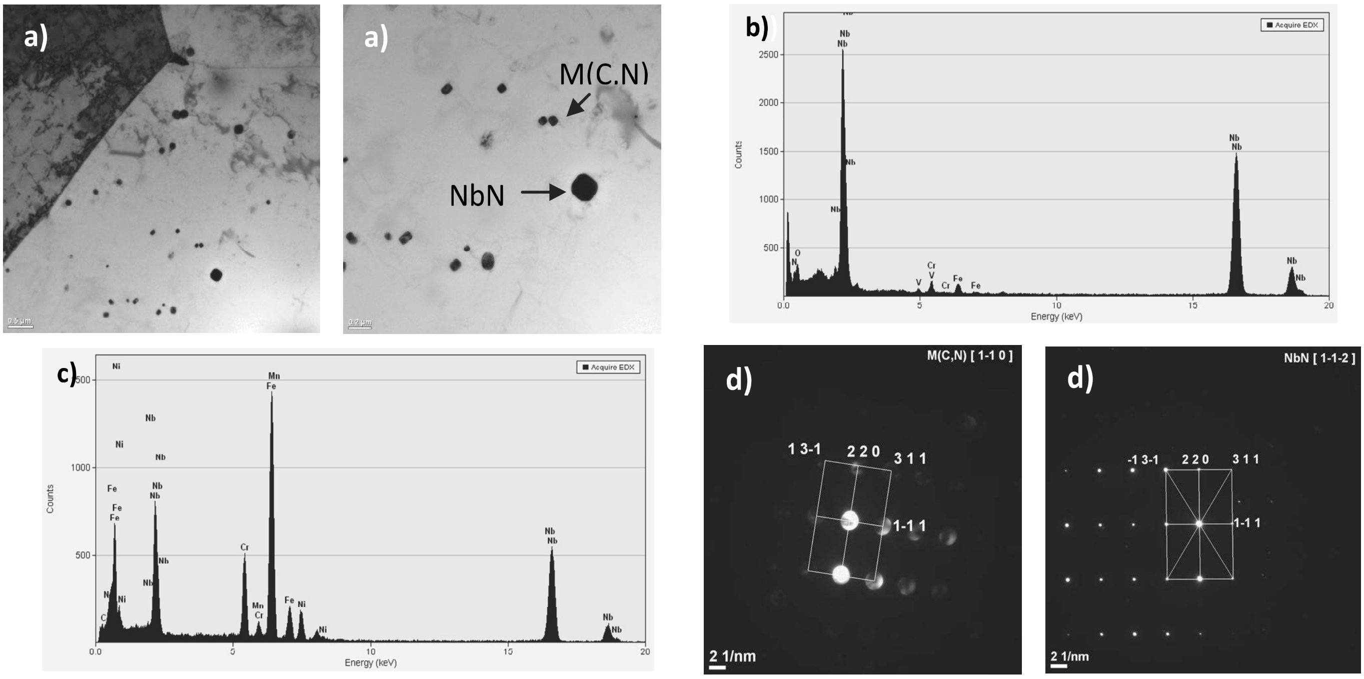

Fig. 15. Microstructure of Super 304H steel in initial state observed with TEM a) bright field, b) EDS spectrum for NbN phase, c) EDS spectrum for M(C,N) phase, d) diffractograms of identified phases

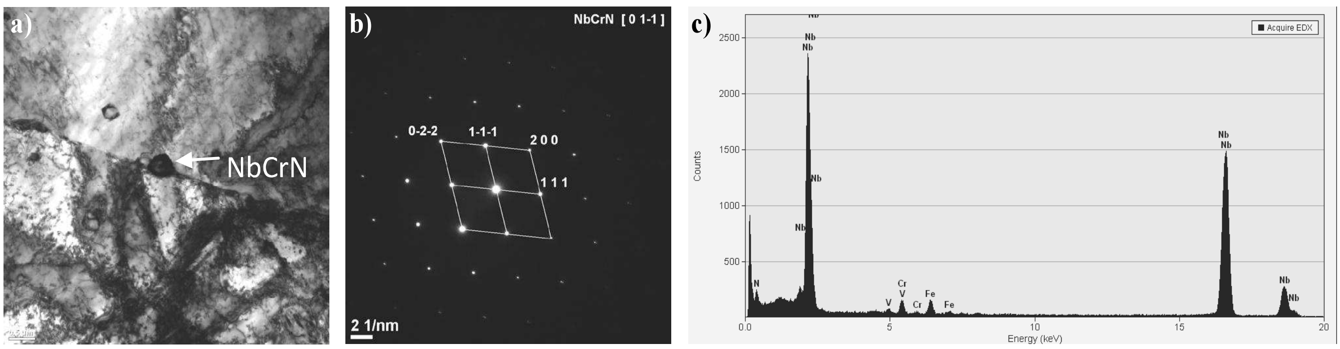

Fig. 16. Microstructure of Super 304H steel after annealing at 700°C for 3000 h observed with TEM a) bright field, b) diffractogram, c) EDS spectrum for NbCrN phase

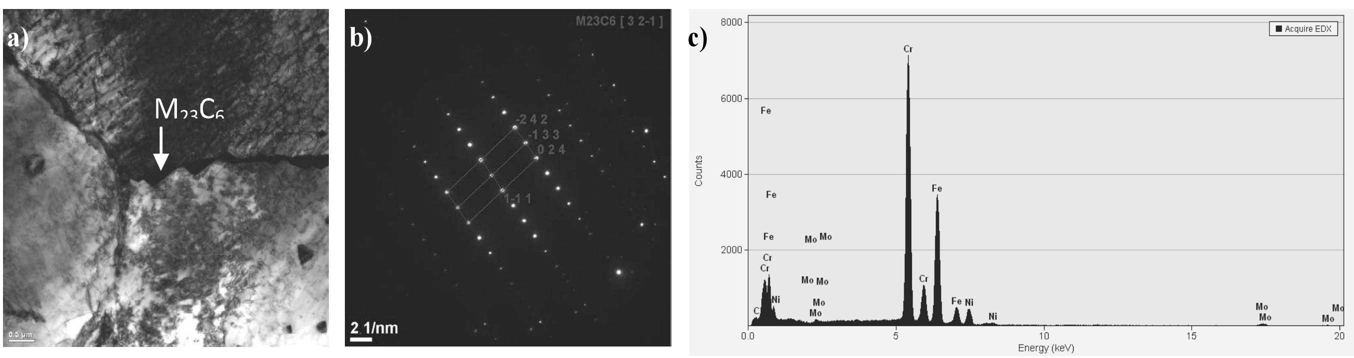

Fig. 17. Microstructure of Super 304H steel after annealing at 700°C for 3000 h observed with TEM a) bright field, b) diffractogram, c) EDS spectrum for $M_{23}C_6$ phase

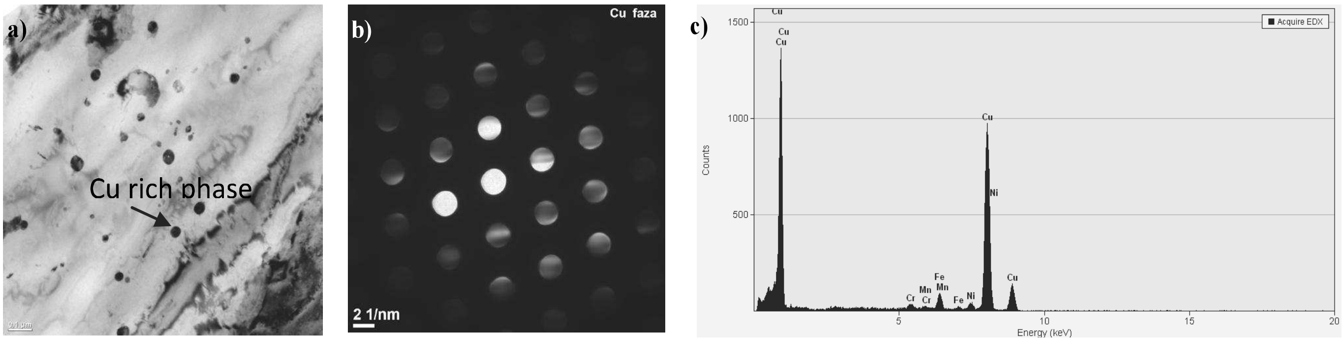

Fig. 18. Microstructure of Super 304H steel after annealing at 700°C for 3000 h observed with TEM a) bright field, b) diffractogram, c) EDS spectrum for phase rich in Cu

4. Conclusions

The literature review and own investigations on HR3C and Super 304H austenitic steels intended for critical elements of boiler in the form of primary and secondary steam superheater coils allow to find out that:

- HR3C and Super 304H steels have similar creep strength within the range of their operating temperatures of 580-650°C, with difference of approx. 10% in favour of Super 304H steel, whereas in case of high exposure to high-temperature corrosion the use of HR3C steel is recommended due to higher chromium content [2],
- in HR3C steel in initial state, the main precipitations are $M_{23}C_6$, NbCrN and MX, while after long-term annealing there may occur the σ phase resulting in loss of mechanical properties,
- in the structure of Super 304H steel in initial state, the main precipitations are NbC and M(C,N). After long-term annealing at 650 and 700°C for up to 5000 hours, the observed structure is austenite with Nb(C,N) carbonitride precipitations both within the grains and at grain boundaries, $Cr_{23}C_6$ carbide precipitations at grain boundaries forming the precipitation chains in places and very fine phase rich in copper.

The steel characteristics presented in this paper are used for assessment of structural changes and changes in strength properties of material of elements after long-term service under creep conditions.

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