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STRUCTURE OF THE S304H STEEL AFTER 20,000 HOURS OF AGEING

The S304H steel is used in the construction of pressure components of boilers with supercritical operating parameters. The paper presents the results of the research on the microstructure after ageing for 20,000 hours at 650 and 700°C. The microstructure examination was performed using scanning and transmission electron microscopy. The precipitates were identifies using transmission electron microscopy. The influence of ageing time on microstructure changes and the precipitation process of the tested steel is described. The presented research results are an element of material characteristics of the new generation of steel, which are used in the design work of pressure devices of steam boilers and in diagnostic work during operation.

Keywords: S304H steel; microstructure; precipitates; ageing; Cu_rich phase; sigma phase

1. Introduction

The basic parameter determining the modernity of a power unit is its efficiency and meeting environmental requirements in terms of the minimum emission of greenhouse gases and harmful pollutants. The use of supercritical steam parameters allows increasing the efficiency of power units to a value above 45%. At the same time, better combustion conditions of solid fuels reduce the emission of pollutants into the air. Hence, the construction of the pressure part of boilers with supercritical steam parameters requires the use of new materials with increasingly higher mechanical properties [1-8]. The critical components of the boiler pressure part include thin-walled steam superheater tubes, whose materials in installations with supercritical parameters can operate at a temperature of up to about 650°C and a pressure of 25-30 MPa. Steels resistant to high-temperature corrosion with austenitic structure, which include the Super 304H steel developed in the 1990s, are being more and more often used for steam superheater components with such high parameters. Table 1 lists units for supercritical parameters of the Polish power industry, where the Super 304H steel is used [9-16].

The S304H (X10CrNiCuNb18-9-3) steel is characterised by high heat resistance and creep resistance, which is 68 MPa at 700°C for 100,000 hours. It is the result of a strong solution and precipitation strengthening [17-19]. Characteristics are developed for the materials from which the boiler components are made in order to obtain knowledge about their behaviour under operating conditions [20-23]. Due to the specific nature of the work of materials used in the power industry, building their characteristics of functional properties is time-consuming and takes several years [17,24,25]. Fig. 1 shows the range of precipitation temperature for the secondary phases of the tested

TABLE 1

Units in operation and under construction for supercritical parameters with superheaters made of the Super 304H steel

Unit location	Power [MW]	Max. pressure PS [bar] – SH/RH	Max working temperature TS [°C] – SH/RH
Bełchatów II PP	860	284/72	569/607
Kozienice PP	1075	266/63	603/621
Opole PP	2 × 950	280/77	603/611
Jaworzno III PP	910	285/59	603/611
Turów PP	460	266/63	603/621

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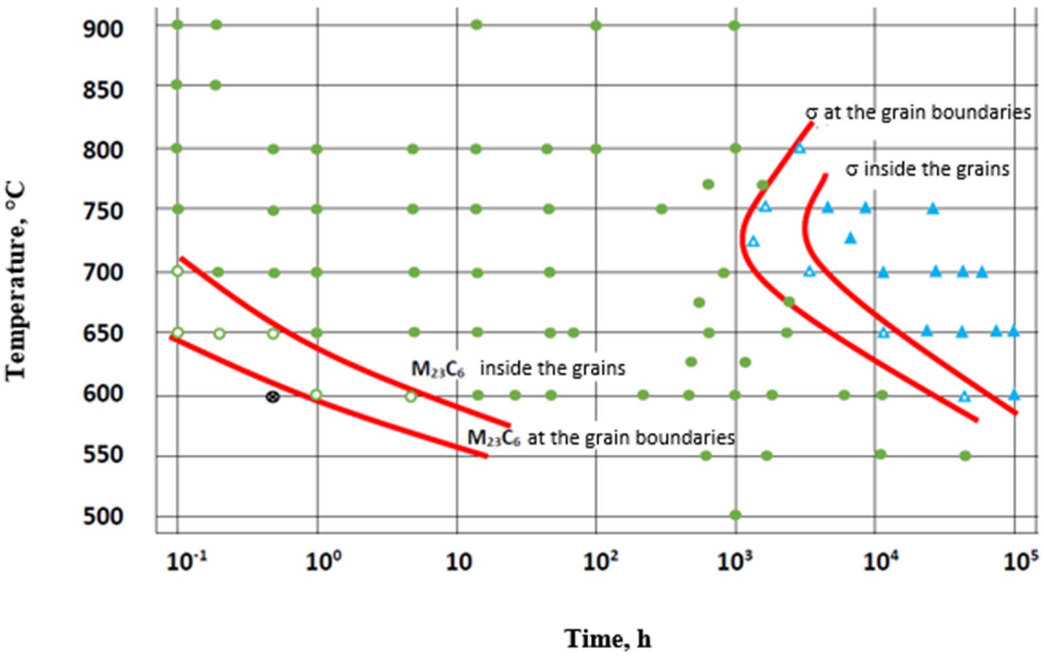

Fig. 1. TTT diagram of secondary phase precipitation ranges in the Super 304H steel

steel. It does not take into account quantitative values and the properties that depend on them [17]. This paper presents an analysis of the results of microstructure tests for the material of a finished component in the form of a steam superheater coil made of the Super 304H steel subjected to ageing up to 20,000 hours.

2. Material for testing

The testing material was a section of a ø 42.4 × 8.8 mm steam superheater coil tube made of the Super 304H steel. The chemical composition of the tested steel in relation to the requirements of the standard is presented in Table 2.

3. Testing scope and methods

The research included the description of the influence of temperature and long-term ageing time on changes in the microstructure of the tested material after 20,000 hours of ageing at 650 and 700°C. The first stage of testing after 10,000 hours is presented in [26].

The observation of the microstructure was carried out using a light microscope, a scanning electron microscope on conventionally prepared electrolytically etched metallographic microsections, and a transmission electron microscope using thin films. The analysis of the precipitation processes was carried out on thin foils with the use of selective electron diffraction. The quantitative analysis of the precipitates was performed using the NIKON EPIPHOT200 & LUCIA G v.5.03 image analysis system. The image analysis system was calibrated using a scale marker on photographs. Calibration coefficient: 1 pixel = 0.040 µm. The tests were carried out on the material after long-term ageing for 20,000 hours at 650 and 700°C.

4. Test results

The microstructure of the as-delivered Super 304H steel (after solution heat treatment) is shown in Fig. 2. The tested material is characterised by an austenitic matrix with visible annealing twins and single primary precipitates of various sizes, located inside the grains. The grain size in the tested steel was 7-9 per ASTM standards.

The ageing of the Super 304H steel at 650 and 700°C for 20,000 h has a significant impact on the development of precipitation processes, which was confirmed by the observation of the microstructure (Figs. 3-5). Along with the longer ageing

TABLE 2

Chemical composition of the material of the tested Super 304H steel tube

	Chemical composition [wt %]											
	C	**Si**	**Mn**	**P**	**S**	**Cu**	**Cr**	**Ni**	**Nb**	**B**	**N**	**Al**
Follow-up	0.09	0.20	0.80	0.003	0.001	2.99	18.40	8.80	0.48	0.004	0.11	0.006
VDTÜV 550:12.2012	0.07 0.13	max 0.30	max 1.00	max 0.040	max 0.010	2.50 3.50	17.0 19.0	7.5 10.5	0.30 0.60	0.001 0.010	0.05 0.12	0.003 0.030

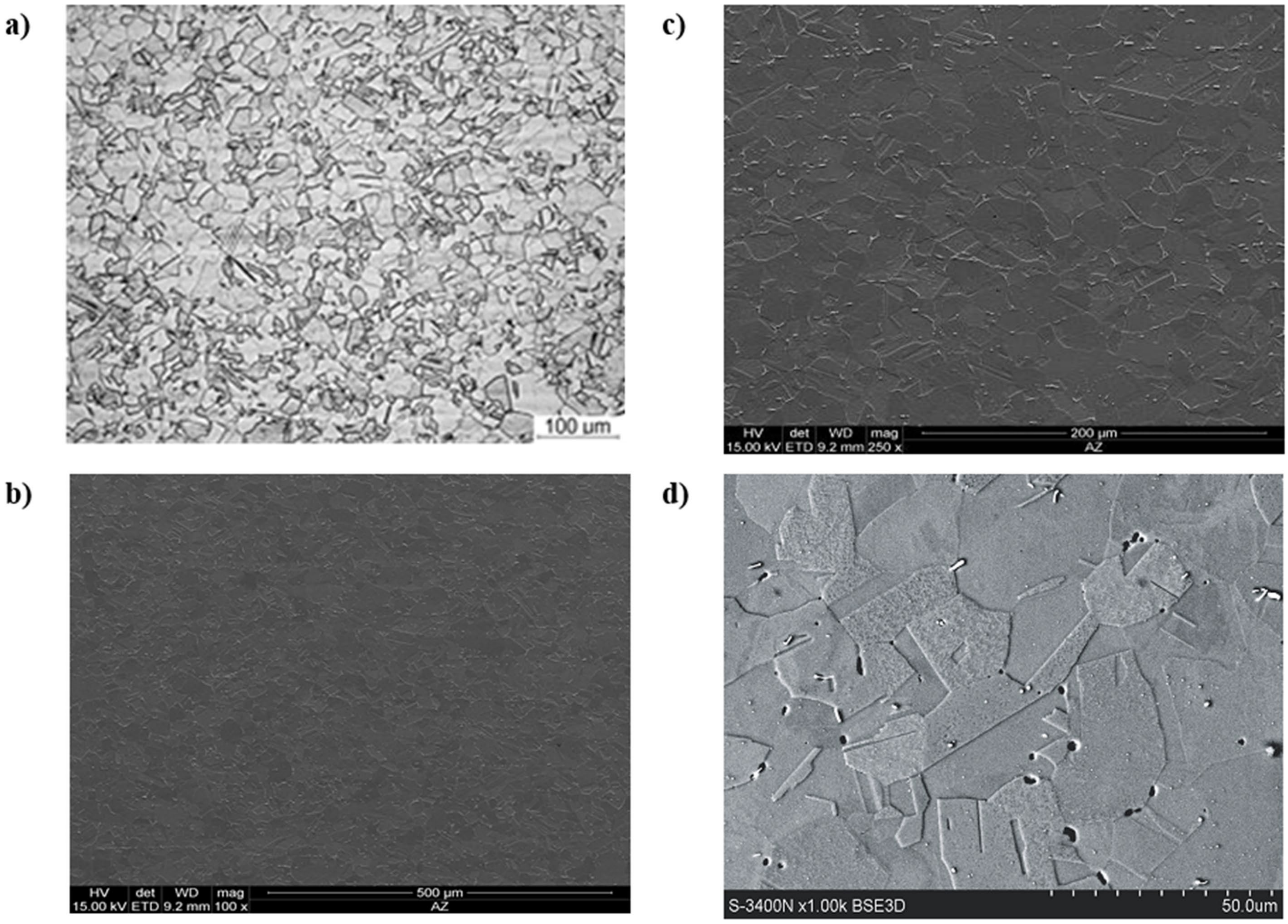

Fig. 2. Microstructure of as-delivered Super 304H steel: a) light microscope LM, b), c), d) scanning electron microscope SEM

time, an increase in the amount and size of $Cr_{23}C_6$ carbides was observed along austenite grain boundaries and annealing twins on the microstructure images. $M_{23}C_6$ precipitates form systems in the form of a lattice along grain boundaries. The examination of the microstructure after ageing for 20,000 hours also showed the presence of the intermetallic σ phase (Figs. 3, 6, 9), the size and percentage of which was much greater in the case of ageing at 700°C, as shown in Figs. 4 and 7, and their summary is presented in Table 3.

The unfavourable σ phase, rich in chromium, is precipitated in austenitic steels during operation above 600°C (Fig. 1). The places which are particularly privileged to its precipitation are

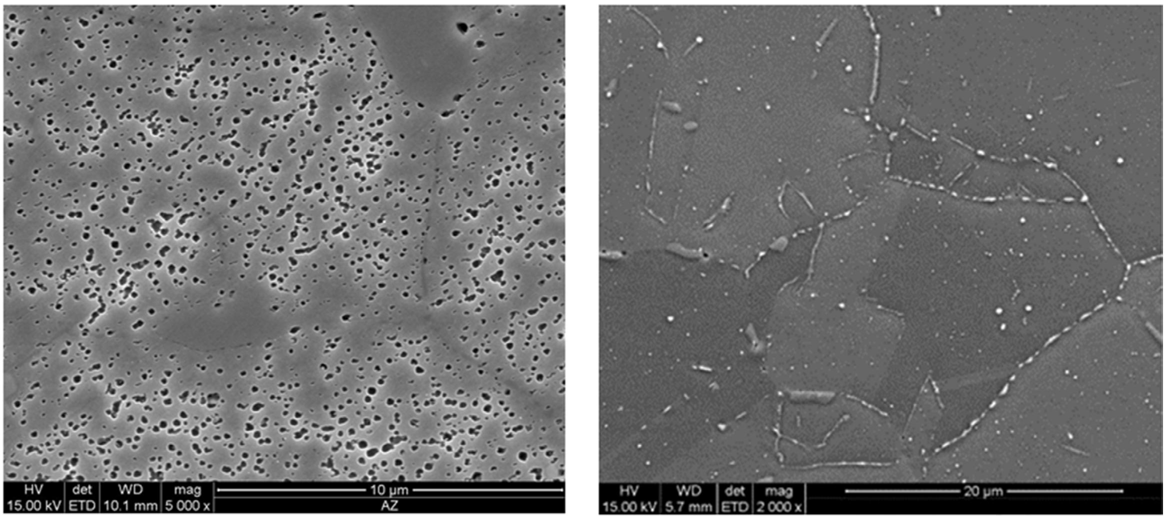

Fig. 3. Microstructure of the Super 304H steel after ageing at 650°C/20,000 h with the precipitates of the ε_Cu phase in a matrix and $M_{23}C_6$ carbides and σ phase along grain boundaries, SEM

TABLE 3

Quantitative analysis of the σ phase in the Super 304H steel

Material condition	Min. diameter µm	Max. diameter µm	Average diameter µm	Standard deviation	Surface fraction %
Ageing 20,000h/650°C	0.65	3.70	1.60	0.55	1.25
Ageing 20,000h/700°C	0.65	6.20	1.74	0.99	2.86

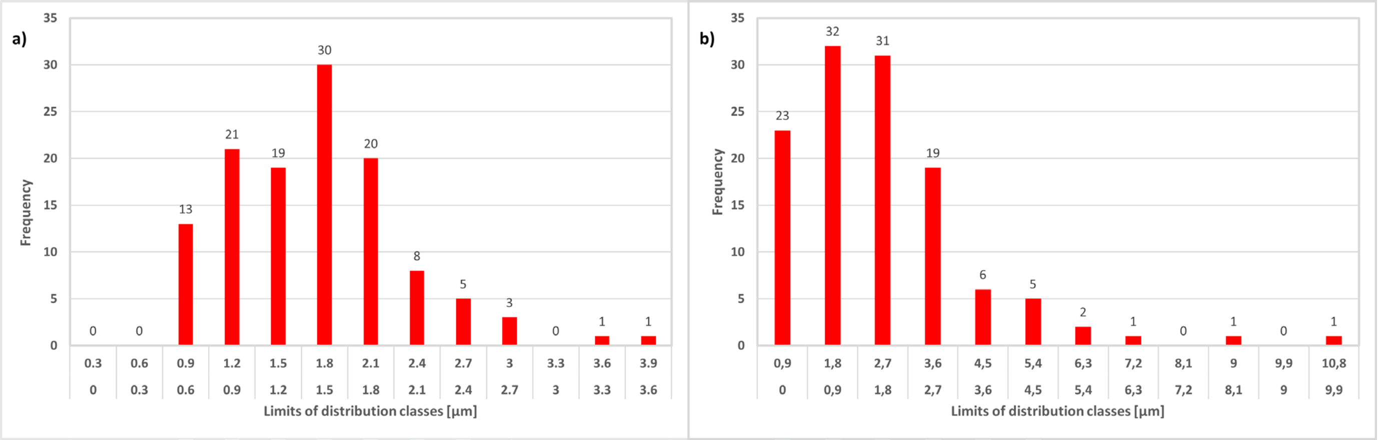

Fig. 4. a) Results of quantitative analysis of the σ phase precipitates equivalent diameter after 20,000 hours of ageing at 650°C, b) Results of quantitative analysis of the σ phase area precipitates after 20,000 hours of ageing at 650°C

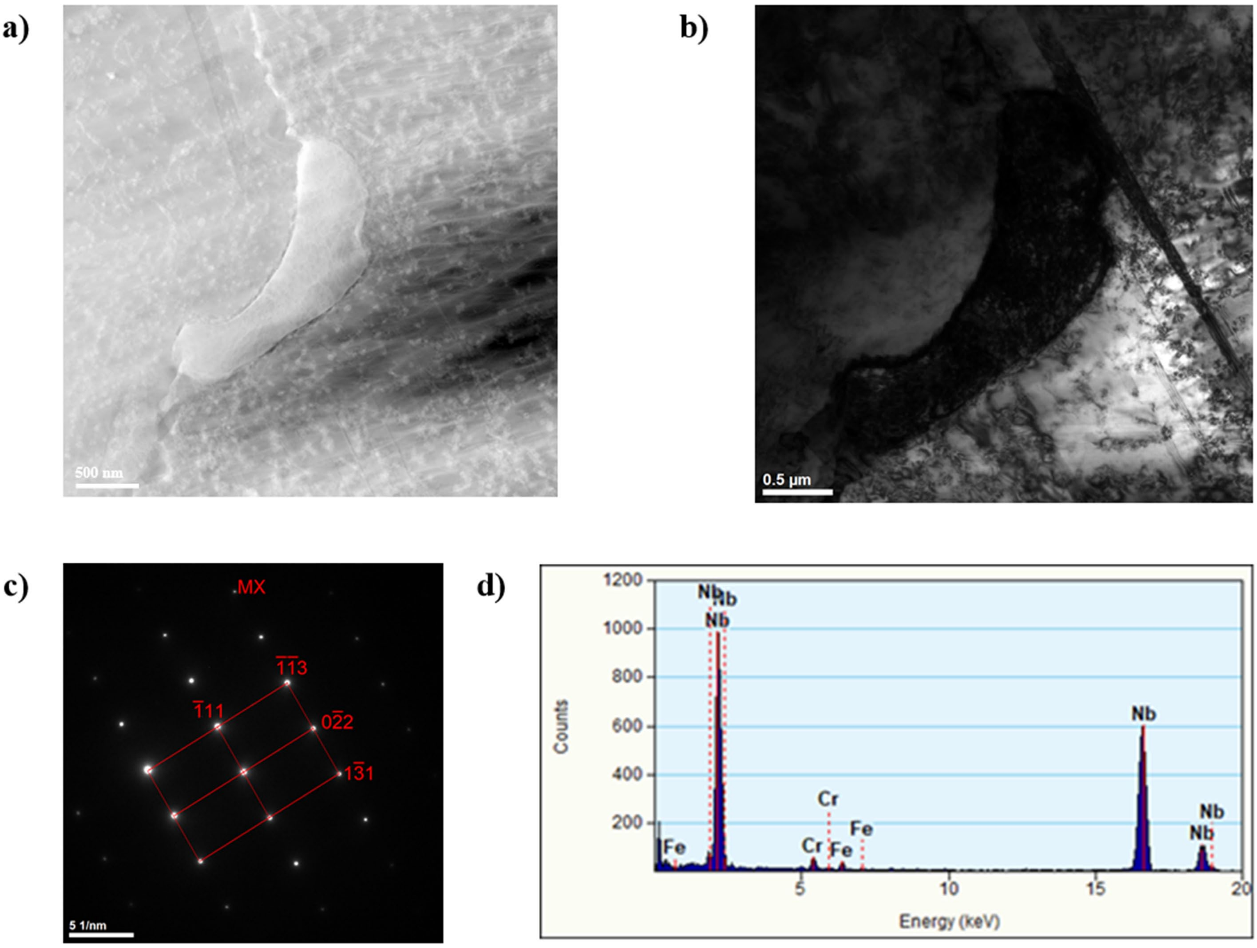

Fig. 5. Precipitates is the S304H steel after ageing at 650°C for 20,000 hours a), b) MX precipitate, c) MX diffraction pattern, d) EDS analysis, TEM

the points of contact of three grains and d ferrite precipitates [17,24]. The precipitation of the σ phase along grain boundaries is accompanied by the dissolution of $Cr_{23}C_6$ precipitates in the matrix. Its precipitation leads to a reduction in plastic properties as well as resistance to oxidation in water vapour and scaling resistance in flue gas atmosphere [3,27].

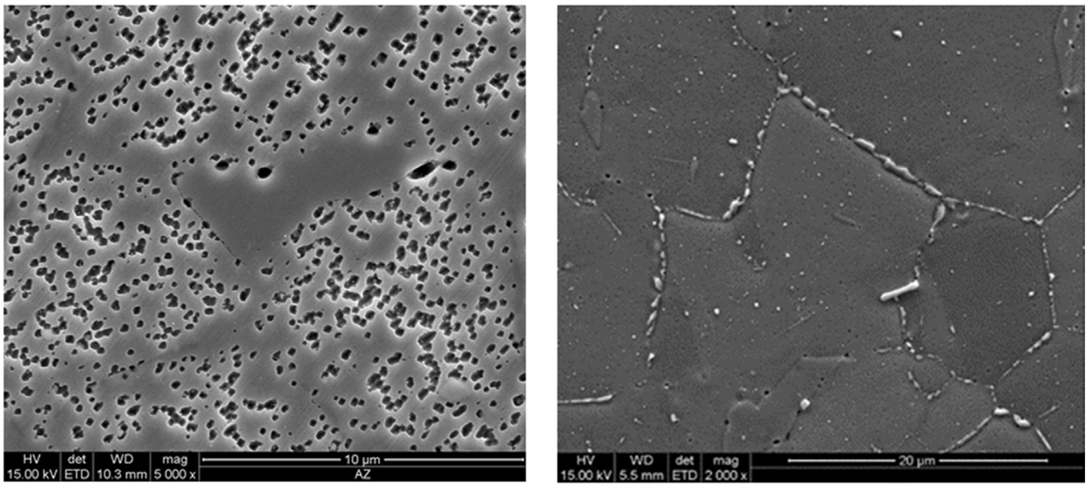

Fig. 6. Microstructure of the Super 304H steel after ageing at 700°C/20,000h with the precipitates of the ε_Cu phase in a matrix and $M_{23}C_6$ carbides and σ phase along grain boundaries, SEM

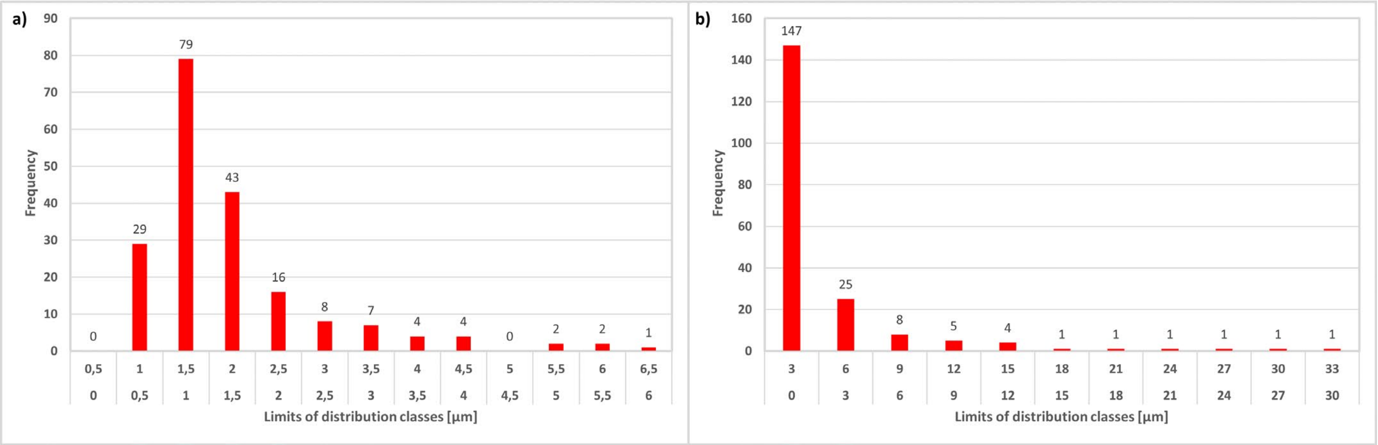

Fig. 7. a) Results of quantitative analysis of the σ phase precipitates equivalent diameter after 20,000 hours of ageing at 700°C, b) Results of quantitative analysis of the σ phase area precipitates after 20,000 hours of ageing at 700°C

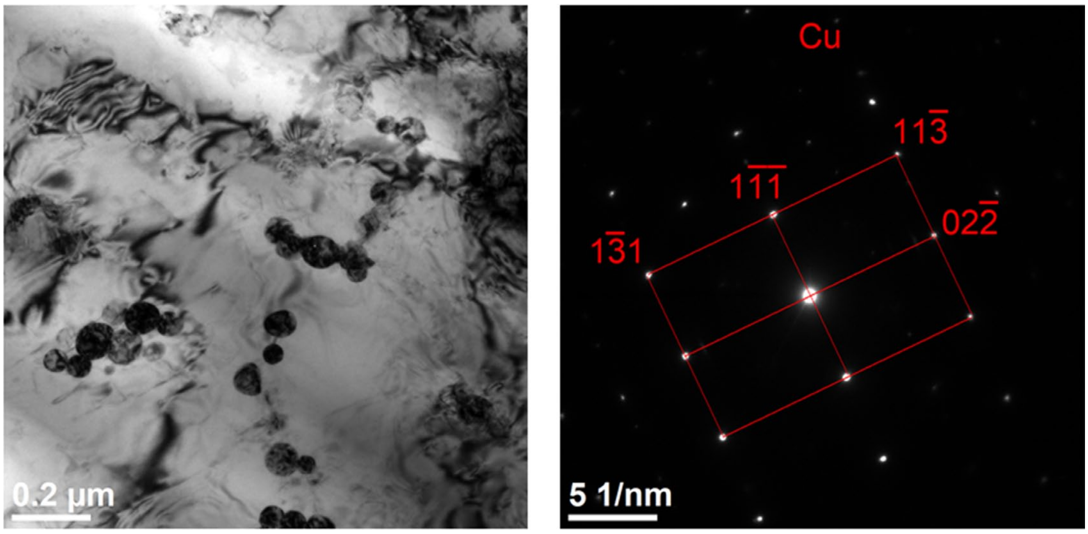

Fig. 8. Copper-rich phase observed using TEM in the S304H steel after 20,000h/700°C ageing

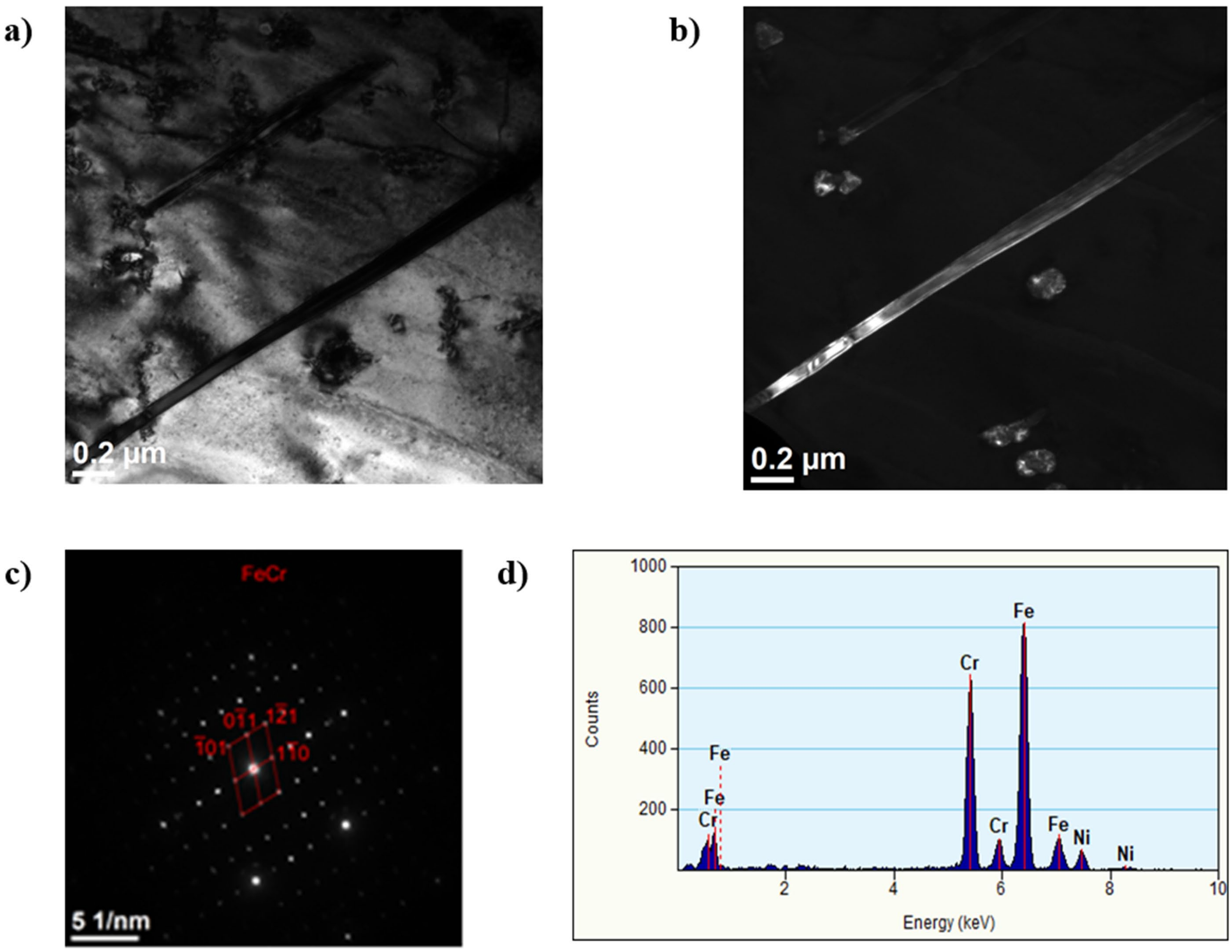

Fig. 9. Precipitates is the S304H steel after ageing at 700°C for 20,000 hours a), b) σ phases, c) σ phase diffraction pattern, d) EDS analysis, TEM

The observation of the microstructure in a transmission electron microscope revealed the presence of very fine MX precipitates (Fig. 5) and a copper-rich phase (Fig. 8) in the tested steel. These phases have the most intense influence on the precipitation strengthening and increase in creep strength. After ageing for 20,000 hours at 650°C, the average diameter of the copper-rich particles in the S304H steel was 39.5 nm. Despite the small volume fraction of the copper-rich phase, amounting to about 3%, it is a very effective obstacle for the free movement of dislocations [17].

5. Summary

Due to high creep resistance at elevated temperature and good resistance to high-temperature corrosion and oxidation in water vapour, the S304H steel is recommended for long-term use under creep conditions at a temperature up to 650-660°C.

The service life of heat-resistant materials, determining their suitability for use at a specific temperature, includes, among others, the results of microstructure stability tests under laboratory ageing conditions at a temperature close to the temperature of the potential application.

The ageing conducted at 650-700°C for up to 20,000 hours revealed significant changes in the microstructure observed in a scanning electron microscope, consisting mainly in the tendency to create an unfavourable morphology, mainly $Cr_{23}C_6$ carbides forming intermittent and continuous carbide systems along grain boundaries and annealing twins, and σ phase precipitates along austenite grain boundaries. Studies using a transmission electron microscope revealed the presence of very fine numerous MX precipitates and a copper-rich phase. Precipitates of this type have a decisive influence on the functional properties of the tested steel during operation at high temperatures.

The presented test results are part of the material characteristics of steels and alloys, enabling, among others, the development of diagnostic procedures in the design and beyond the design working time of steam boiler components operating under creep conditions.

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