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Microstructural and mechanical properties changes of T321H steel after long time creep service

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Materials

ABSTRACT

Purpose: Characteristics of changes in properties and structure of austenitic-matrix steels in delivery state and after long-term service.

Design/methodology/approach: For selected degradation states of T321H steel the mechanical testing and 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 elements in the pressure section of power boilers were summarised in a single paper.

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

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

Keywords: Structure; Mechanical properties; Austenitic steel T321H

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1. Introduction

The development of power technologies is involved, among other things, with construction of power units for increased supercritical steam parameters. The increase in steam temperature from 540 to more than 650°C and pressure from approx. 18 to 30 MPa considerably improves the efficiency of power units from approx. 33 to 40-50% with simultaneous reduction in emission of harmful substances, mainly CO_2, SO_2 and NO_x, to the atmosphere. The development of power technologies is determined by the development of materials engineering. New materials must meet high requirements for proper creep strength and resistance to high-temperature corrosion in waste gas atmosphere and oxidation in steam, and they should also demonstrate satisfactory technological properties with regard to welding, bending and heat treatment. It mainly concerns the critical elements of boiler, which include steam superheater coils, steam pipelines, collectors and sheet pile walls of boiler. Depending on the temperature range of operation, low- and high-alloy ferritic-based (bainitic and martensitic) steels, Cr-Ni austenitic steels with micro-additives including, but not limited to, Nb, V, Ti, N, B and nickel superalloys are used for elements of modernised and newly constructed boilers [1,2,3] (Fig. 1). In Poland, three power units are being operated at present and their coils at the last step of steam superheater are made of austenitic steel, however their service time does not exceed 15 thousand hours. The investment plans include three other units for supercritical parameters (PGE Opole, ENEA Kozienice, Jaworzno III power stations) where austenitic steels will be used. The knowledge and experience in use of austenitic steels is low. Hence, it is extremely important to acquire knowledge of development of structure and property degradation processes and find out about the cause and effect relationships related to durability of austenitic steel structural components during long-term service under creep conditions.

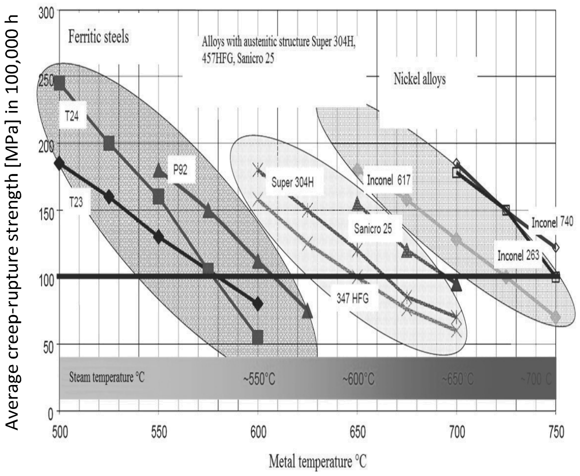

Fig. 1. Steels and alloys to be used for boiler elements

For conventional ferritic-based materials the degradation criteria have been created to be used for assessment of suitability of such steels for further operation [4,5,6]. Thus, at the age of development of boilers with supercritical and USC working parameters, it is extremely important to carry out the preceding research and develop the degradation degree assessment criteria for austenitic steel, similarly to ferritic steels.

2. Material for investigations

The subject of investigations is selected test pieces of steam superheater coils with outside diameter of ø44 mm and wall thickness of 7 mm made of 321H steel (according to ASTM, tab. 1), sampled at AMOS Power Station, USA, operated since 1973, and delivered by the Energy Power Research Institute (EPRI), Charlotte, USA. Depending on the superheating degree, the tested pieces were operated at steam temperature between 540 and 560°C and pressure of 25 MPa for 150,000 to 207,000 hours. [7]. The nominal chemical composition of T321H steel as compared to other austenitic steels used in boilers for supercritical parameters is summarised in Table 1 [8].

Fours test pieces after service (marked 13, 17, 20 and 21) and one test piece in as-received state were selected for investigations.

3. Purpose and range of testing

The main aim of conducted tests of T321H steel in initial state and after various service times is to analyse changes in microstructure and properties and build the microstructure evolution model and criteria to allow forecasting the lifetime of steam superheater coils made of steels with similar chemical composition in the future. The professional literature does not provide explicit procedures and objective criteria useful for residual assessment of austenitic steels such as those used in the engineering practice with regard to high-temperature creep resisting ferritic-matrix steels [9]. The preliminary proposal in this respect is presented in joint publication [10-15].

The scope of the work includes:

- investigation of basic mechanical properties at room temperature,
- investigation of microstructural changes with assessment of development of carbide precipitation processes observed with light, scanning and transmission electron microscope,
- investigation of precipitation processes using X-ray diffraction analysis of electrolytically isolated precipitations,
- creep tests for material in initial state and after long-term service were also started.

4. Test results

4.1. Strength properties

The investigations of mechanical properties of material in as-received state and after long-term service, i.e.: tensile strength TS, yield point YP, elongation A and reduction of area Z, were carried out at room temperature and their results are summarised in Table 2, while comparison of test results for these properties after service under creep conditions and in as-received state are presented in Figs. 2-5.

Tensile strength of T321H steel steam superheater pipe test pieces after long-term service for which accurate service times are not available is diverse (Fig. 2). Tensile strength of material in as-received state is on average 567 MPa and after service it varies between 487 and 630 MPa, while yield point for material of tested pieces is lower than that of material in as-received state by max 30% (Fig. 3).

The measurements of elongation and reduction of area in static tensile test (Figs. 4, 5) indicate that after service these properties are lower than in as-received state by approx. 35 for elongation A5 and approx. 45% for reduction of area. Nevertheless, the obtained values of elongation and reduction of area amounting to approx. 36% indicate that these properties for tested 321H steel pieces after service for 150,000-200,000 hours are still high.

In addition, Vickers hardness measurements were taken on tested pieces of steam superheater coils (Tab. 3).

Hardness of steam superheater coil material of tested T321H steel, which was approx. 140 HV10 in initial state increased to 167 HV10 after long-term service.

The results of hardness measurements (Table 3) are well correlated with changes in values of yield point and tensile strength as well as with plastic properties determined in static tensile test (Figs. 2-5). The increase in both mechanical properties and hardness is the effect of numerous fine precipitations inside austenite grains due to ageing.

Table 1.
Chemical composition of austenitic steels used in construction of supercritical boilers [8]

Grade	Chemical composition							Maximum temperature of long-term service according to PN-EN 12952_1:2004
	C	Si	Mn	Cr	Ni	N	Others	
1	2	3	4	5	6	7	8	9
T321H	**0.04-0.08**	**max 1.0**	**max 2.0**	**17.0-19.0**	**9.0-12.0**	**-**	**Ti:max 0.8**	**620°C**
TP347HFG	0.06-0.10	max 0.75	max 2.0	17.0-19.0	9.0-13.0	-	Nb: max 1.0	620°C
Super 304H	0.07-0.13	max 0.30	max 1.0	17.0-19.0	7.5-10.5	0.05-0.12	Cu: 2.5-3.5 Nb: 0.3-0.6	645°C
HR3C	0.04-1.0	max 1.50	max 2.0	23.0-27.0	17.0-23.0	0.15-0.35	Nb: 0.2-0.6	670°C

Table 2.
Results of static tensile test of material in as-received state and after service

Material condition	Symbol	TS, MPa	YP, MPa	E, %	Z, %
1	2	3	4	5	6
initial state	**10**	**567**	**268**	**57**	**64**
after long-term service under creep conditions	13	630	245	36	34
	17	487	187	36	34
	20	578	250	40	37

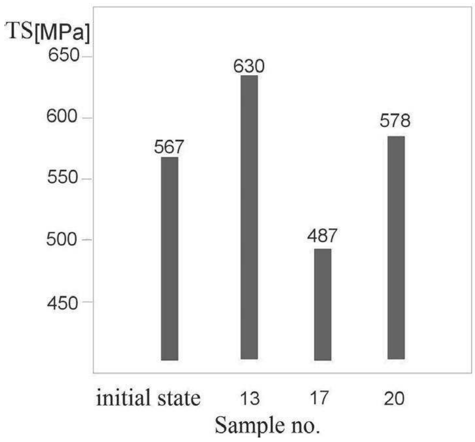

Fig. 2. Comparison of tensile strength at room temperature for material in as-received state and after long-term service under creep conditions

4.2. Assessment of material microstructure of test pieces of T321H steel steam superheater coils

The microstructural investigations were carried out with light microscope as well as scanning electron microscope (with magnification of up to 5000 x) and transmission microscope using thin-foil technique.

The T321H steel in as-received state is characterised by homogeneous austenitic structure containing twins with grain size of 6-8 according to ASTM and few TiC primary carbides with characteristic regular shapes (Fig. 6). The structural investigations of materials after long-term service under creep conditions revealed the diverse degree of secondary phase precipitation process advancement (Figs. 7-10). This diversity is probably the result of real temperature and service time parameters. In addition to service time, the main parameter that determines the dynamics of changes occurring in structure and morphology of precipitating secondary phases is the real working temperature. In material of tested pieces after long-term service under creep conditions, first of all the numerous evenly distributed fine $M_{23}C_6$ carbide precipitations inside austenite grains and few precipitations at grain boundaries were revealed. In addition, in microstructure of all the three tested pieces the diverse degree of populating grain boundaries with σ phase (FeCr) (Figs. 8-10) as well as the existence of dispersive TiC carbide precipitations at dislocations (Fig. 10) were observed.

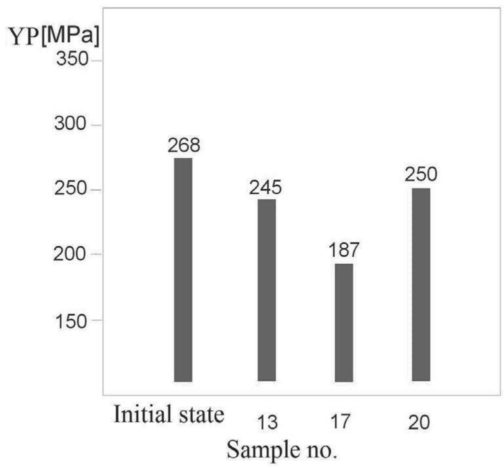

Fig. 3. Comparison of test results of yield point at room temperature for material in as-received state and after long-term service

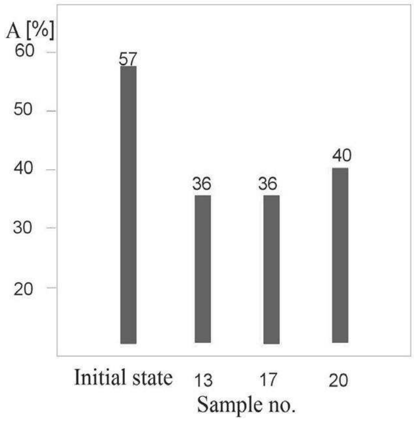

Fig. 4. Comparison of measurement results of elongation at room temperature for material in as-received state and after long-term service

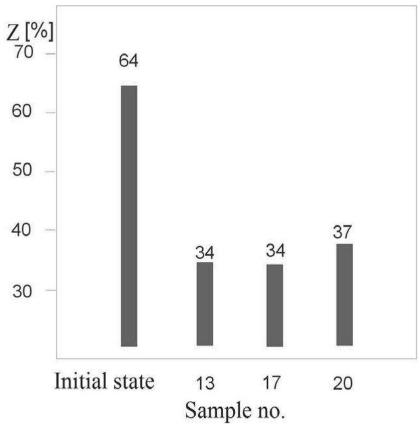

Fig. 5. Comparison of test results of reduction of area at room temperature for material in as-received state and after long-term service

Table 3.
Results of HV10 hardness measurement for material of steam superheater coils in initial state and long-term service

Material condition	Symbol	HV10 hardness
1	2	3
initial state	**10**	**138**
after long-term service under creep conditions	13	167
	17	156
	20	152

The further stage of development of the precipitation process probably triggered off by temperature and extended time of service is connected with coagulation and growth of $M_{23}C_6$ carbides inside and at austenite grain boundaries. At the same time, the σ phase precipitation growth process intensifies at austenite grain boundaries and these precipitations locally form a discontinuous and even continuous network (Figs. 9, 10). In the near-boundary zone of continuous σ phase network, the area free of $M_{23}C_6$ carbides was observed, at the expense of which the growth of σ phase at grain boundaries took place (Fig. 8).

The characteristic feature of austenite substructure in all the three tested states of 321H steel after service is relatively high morphology stability of dispersive TiC carbide precipitations.

The existence of TiC and $M_{23}C_6$ carbides and σ phase is confirmed by the results of observation of thin foils on the material of test piece marked with no. 20 using the transmission electron microscope with magnifications between 15 and 100 thousand (Fig. 10) and the results of X-ray diffraction analysis of deposit of precipitations isolated electrolytically from the material of test pieces taken from steam superheater coil marked with no. 13 and 17 (Figs. 11, 12).

a)

b)

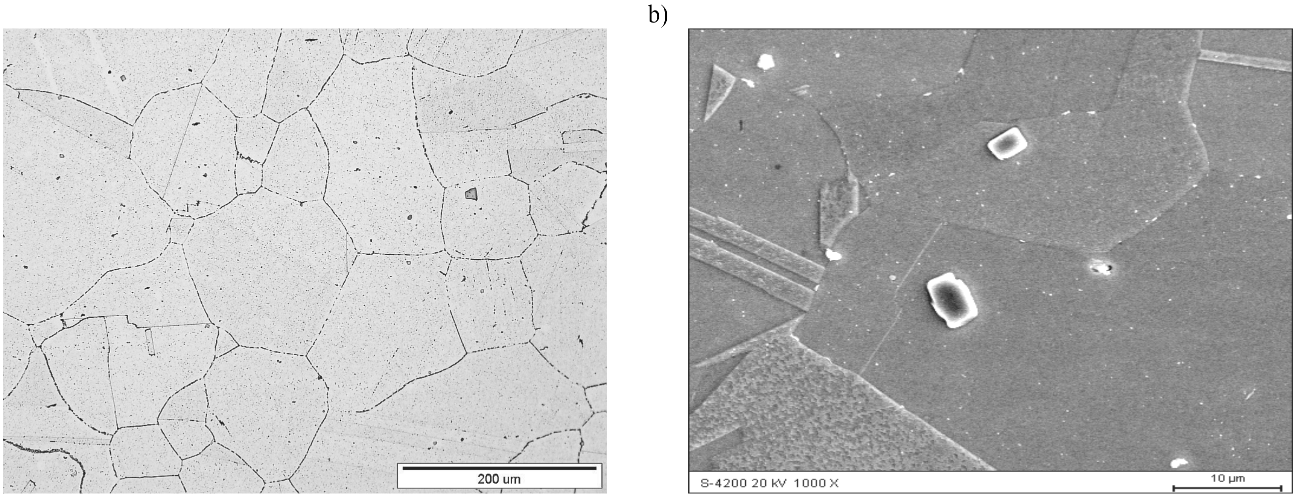

Fig. 6. Microstructure of material of steam superheater coils of T321H austenitic steel in as-received state (test piece no. 10) observed with a) light microscope, b) SEM

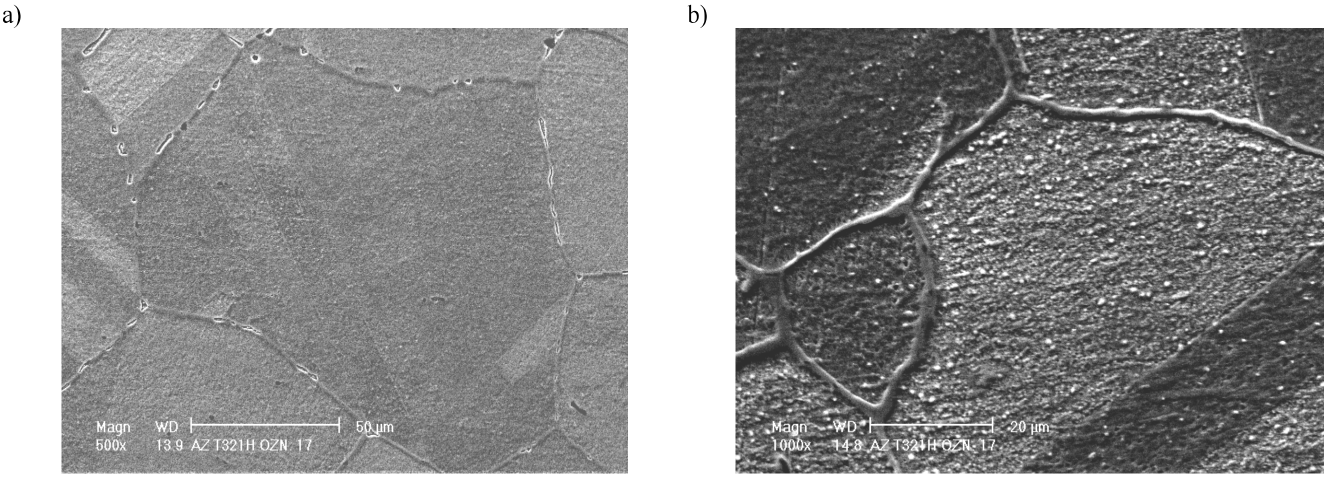

Fig. 7. Example of typical homogeneous austenite microstructure with fine M23C6 carbide precipitations in material of steam superheater coil no. 17 observed with SEM

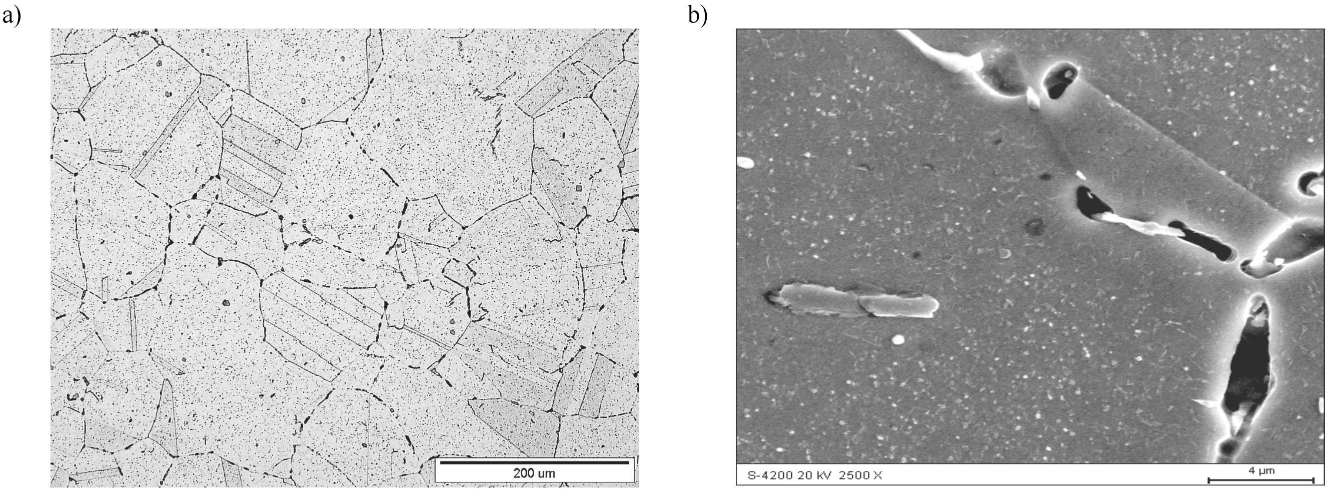

Fig. 8. Microstructure of austenite from test piece of steam superheater coil (no. 17). a) LM, b) Detail with chipped $M_{23}C_6$ carbides at sigma phase boundary. Dispersive TiC particles in matrix

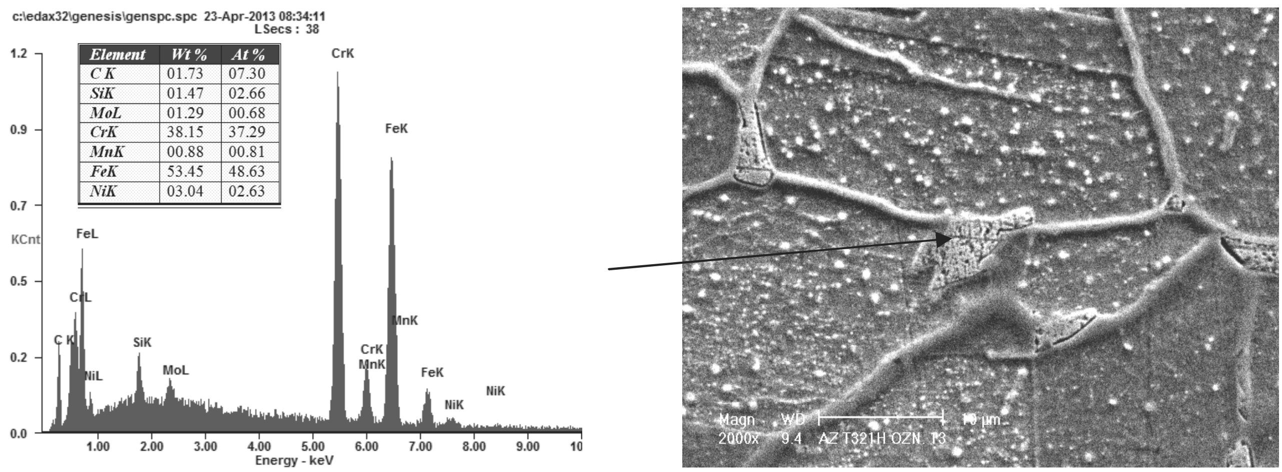

Fig. 9. Typical networked microstructure of steam superheater coil material marked with no. 13, with conglomerates of sigma phase and carbides

a) b)

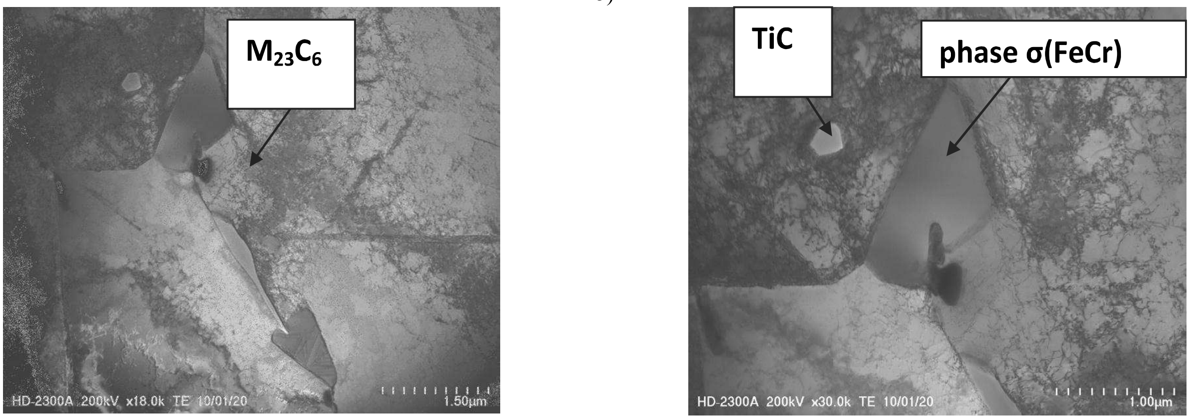

Fig. 10. Austenite substructure in 321H steel of superheater coil test piece marked with no. 20 after long-term service, TEM, thin foil. a) $M_{23}C_6$ carbides at austenite grain boundary with dispersive TiC carbides, b) fragment of continuous sigma phase network with $M_{23}C_6$ carbides and dispersive TiC precipitations in matrix

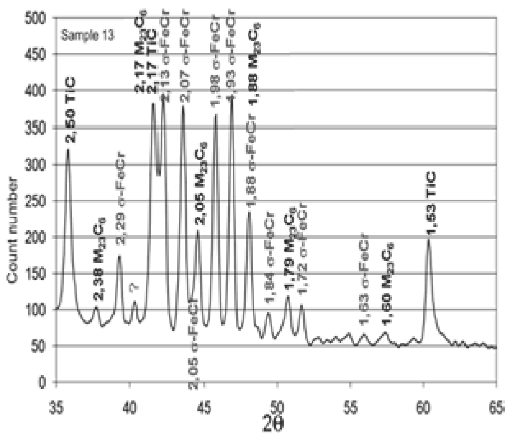

Fig. 11. X-ray diffraction analysis of deposit of precipitations isolated electrolytically from material of T321H austenitic steel steam superheater coil test piece after long-term service under creep conditions (test piece no. 13)

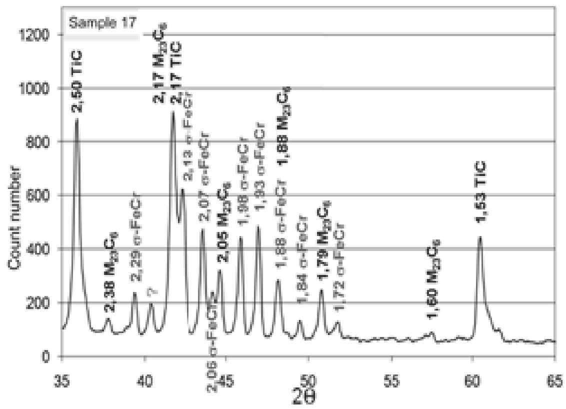

Fig. 12. X-ray diffraction analysis of deposit of precipitations isolated electrolytically from material of T321H austenitic steel steam superheater coil test piece after long-term service under creep conditions (test piece no. 17)

The obtained test results become the part of proposed structure degradation model shown in Fig. 13 [6,7]. This model will be verified and supplemented with methodology for condition assessment of tested steel operating under creep conditions based on the assessment of changes in structure related to degree of exhaustion.

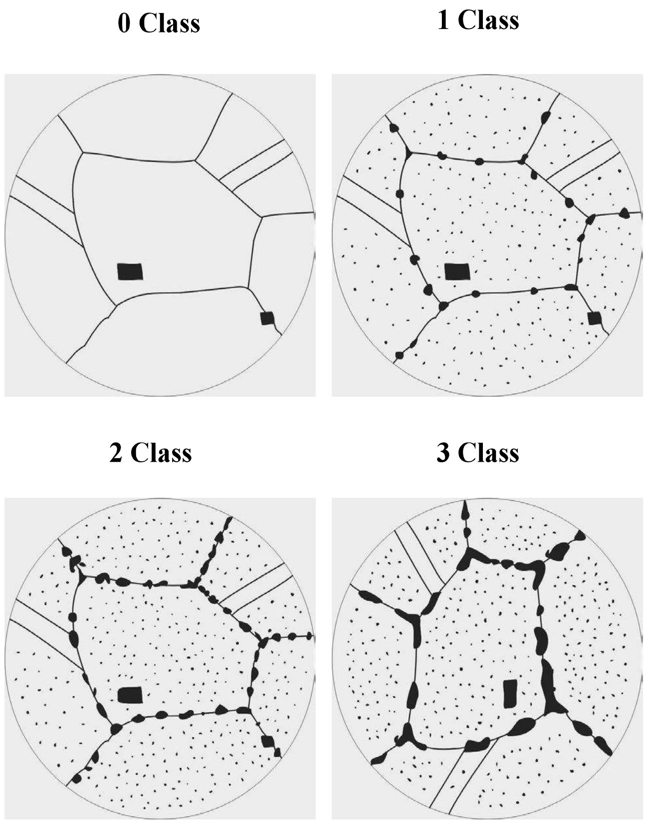

Fig. 13. Proposed preliminary structure degradation model for 321H steel after service under creep conditions with no internal damages

5. Conclusions

The investigations of T321H austenitic steel in initial state and after long-term service under creep conditions conducted so far have revealed that:

- Tensile strength of T321H steel after long-term service as compared to that obtained for initial state increases in the initial period of operation and precipitation reinforcement reaching the value of 630 MPa. The extension of service time and impact of elevated temperature intensifies the precipitations of secondary phases and affects changes in precipitation morphology resulting in decreasing both tensile strength and yield point by approx. 30%. At the same time, the reduction in plastic properties (elongation and reduction of area) to approx. 35% is observed, which is still a very satisfactory value.

  Hardness of steam superheater coil material of tested T321H steel, which was approx. 140 HV10 in initial state increases to approx. 165 HV10 after long-term service.

  The increase in mechanical properties as well as hardness is the effect of numerous fine precipitations of $M_{23}C_6$ and TiC carbide inside austenite grains and the reduction in plastic properties is caused by the change in morphology of precipitations with predominating σ phase at austenite grain boundaries as a result of long-term ageing.
- The microstructural investigations of materials after long-term service under creep conditions revealed diverse degree of the advancement of precipitation processes as from the initial state of structure after solutioning.
- The following phases occur in austenitic microstructure of tested T321H steel after long-term service: few primary TiC carbides with regular shapes, dispersive TiC precipitations, $M_{23}C_6$ carbide and sigma phase. The presence of sigma phase in the structure was found in all of the tested pieces after long-term service.
- The electrochemical phase isolation and X-ray phase analysis reveal, by means of the intensity of diffractions peaks, semi-quantitative diversity in the share of individual phases whose total mass fraction in tested samples ranges between 2.29 and 3.99 %wt.

  This diversity is the result of real parameters of completed operation. In addition to service time, the main parameter which determines the dynamics of changes occurring in the structure is the level of real working temperature. The higher the real working temperature is the bigger the structural changes after similar service time are. It is not impossible that some coils were replaced with new ones during the time of complete 200,000 h service of boiler from which the test pieces were taken for investigations.
- Based on the test results of selected test pieces of steam superheater coils, the sequence of microstructural changes during long-term service with regard to secondary phase precipitation processes can be defined and used to distinguish four model classes for condition of evolved microstructure from as-received state (Fig. 13).
- The first stage of precipitation processes is probably connected with precipitation and uniform distribution of $M_{23}C_6$ carbides inside austenite grains and partially at boundaries (class 1). Further changes in microstructure should be associated with coagulation/growth of $M_{23}C_6$ carbide precipitations both inside grains and at grain boundaries and with initiation of σ phase (FeCr) precipitation, mainly at grain boundaries (class 2). Precipitation of sigma phase is to a large extent conditioned by presence of $Cr_{23}C_6$ carbide, which is shown by the results of microstructure observation with SEM and TEM (Figs. 8-10). Long-term service under creep conditions also results in development of precipitation of dispersive TiC particles, mainly at dislocations (Fig. 10), which is indicated by observations of thin foils with TEM, but also by diverse intensity of diffraction peaks from TiC (Fig. 12). Few primary precipitations of TiC carbide are stable and their presence may affect the generation of creep voids at their boundaries.
- The final stage of ageing processes during long-term service is presented by microstructure with predominating content of sigma phase, which locally forms the continuous network along grain boundaries (class 3) and coagulated $M_{23}C_6$ carbides nearby sigma phase as well as fine precipitations inside grains. The condition of microstructure with continuous network of sigma phase at grain boundaries can be considered as one of the main criteria of material degradation during long-term service.
- The obtained results of mechanical and microstructural investigations of material after long-term service imply that the decisive criterion for material degradation and extended lifetime will be the state of development of creep damages.

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