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THE EFFECT OF LONG-TERM IMPACT OF ELEVATED TEMPERATURE ON CHANGES IN MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HR3C STEEL

The HR3C is a new steel for pressure components used in the construction of boilers with supercritical working parameters. In the HR3C steel, due to adding Nb and N, the compounds such as MX, CrNbN and $M_{23}C_6$ precipitate during service at elevated temperature, resulting in changes in mechanical properties. This paper presents the results of microstructure investigations after ageing at 650, 700 and 750 °C for 5,000 h. The microstructure investigations were carried out using scanning and transmission electron microscopy. The qualitative and quantitative identification of the existing precipitates was carried out using X-ray analysis of phase composition. The effect elevated temperature on microstructure and mechanical properties of the examined steel was described.

keywords: HR3C steel, high temperature aging, microstructure, mechanical properties

1. Introduction

In the light of the European legal conditions, domestic brown and hard coal stocks, decapitalisation of most power units operated in Poland and energy security, the research and development directions aim at construction of modern power units with supercritical working parameters of up to 620 °C and 18 MPa and, in the near future, with ultra-supercritical steam parameters, i.e. 650-740 °C and 30-35 MPa [1-3].

It is widely recognised that fossil fuels, in particular coal, will remain the main source for production of electric energy in the decades to come, whereas the plans of the construction of nuclear power plants, according to the latest data from the Ministry of Economy, is the year 2030 [4].

To reduce the CO_2 level in the atmosphere and save fossil fuels, it is necessary to improve the efficiency in the electric energy production. It allows the development of new steels and alloys for service at elevated and high temperatures [5-10].

The history of construction of supercritical boilers dates back to the 1950s [1]. It was then that the first prototype power units with parameters of the order of 30MPa/649/566 °C were built in USA, at Eddystone Power Plant, a member of Philadelphia Electric Co, and in Ukraine [11]. The basic austenitic steels and technologies, which failed to meet the quality requirements, were used then. The technological errors caused by the lack of experience and insufficient state of knowledge of austenitic steels and the way of their use resulted in large service problems and low availability of the units. Only in the mid-1990s, the supercritical power units were returned to.

The materials used for construction of boiler components must ensure stable behaviour of mechanical properties: yield point, creep strength, low susceptibility to increase in brittleness, resistance to corrosion within up to 200,000 h. It is possible by maintaining stable structure and physical properties during service. It should be noted that such parameters are constantly reduced during service. Yet they should not be lower than the acceptable lower limit as determined at the design stage [12-15].

In addition to high mechanical properties, these materials should be characterised by good weldability, ability to cold and hot strains, and also by non-complex heat treatment.

At present, in Poland and across the world, not only martensitic-matrix steels, but also high-nickel and high-chromium austenitic steels, such as HR3C, Super 304H, HR6W, and CR30A, as well as nickel superalloys, such as Inconel 617, 625 and 740, are within the area of interest in materials for construction of modern boilers [1,16-20]. The use of these materials for construction of boilers requires not only high mechanical properties, but first of all the assessment of their behaviour during long-term service [21-22].

2. Research methodology and material for investigations

The material for investigations was new-generation high-temperature creep resisting austenitic steel HR3C (X6CrNiNbN25-20) intended for use in elements of boilers with super- and ultra-supercritical steam parameters. The HR3C grade is a corrosion-resistant chromium-nickel austenitic steel with medium chromium content of approx. 25% Cr, 20% nickel and with addition of niobium and nitrogen.

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TABLE 1

Chemical composition of HR3C steel under investigation, %

Material	Chemical composition [%]								
	C	Si	Mn	P	S	Cr	Ni	Nb	N
As tested	0.06	0.39	1.15	0.013	0.002	18.41	20.15	0.47	0.23
Vd TUV546	max. 0.10	max. 1.50	max. 2.00	max. 0.03	max. 0.03	23.00 27.00	17.00 23.00	0.20 0.35	0.15 0.35

It is characterised by high creep strength compared to other high-alloy steels, which is 66 MPa at 700 °C for 100,000 h. It is the effect of solution and precipitation hardening of this steel. The creep strength value is a good recommendation for its use in boilers with supercritical working parameters. High chromium content provides very good resistance to high-temperature corrosion and oxidation in steam atmosphere. Chemical composition of the steel under investigation with reference to the requirements of the standard is presented in Table 1. The test pieces were sampled from the sections of finished products in the form of tubes with dimensions of ϕ 54x4.4 mm.

The microstructure investigations were carried out using Inspect F scanning electron microscope (SEM) on conventionally prepared metallographic microsections etched with ferric chloride and TITAN 80-300 transmission electron microscope (TEM) using thin foils. The analysis of precipitation processes was carried out by X-ray analysis of carbide isolates with Philips diffractometer and by means of thin foils using selective electron diffraction.

The investigations of mechanical properties of HR3C steel in the as-received condition and after long-term ageing included the static tensile test at room and elevated temperature using Zwick testing machine with max stress of 200 kN, hardness measurement by Vickers method with Future – Tech FM – 7 hardness testing machine using the indenter load of 10 kG and impact test on V-notched test samples.

The quantitative analysis of precipitations was carried out using the image analysis system NIKON EPIPHOT200 & LUCIA G v.5.03. The scale marker as shown in the photos was used for calibration of the image analysis system. Calibration coefficient: 1 pixel= 0.040 μm.

The above-mentioned tests were carried out on the material in the as-received condition and after long-term ageing at 650 and 700 °C for 1,000 and 5,000 h.

3. Research results and discussion

3.1. Microstructure

The microstructure of HR3C steel in the as-received condition observed with scanning electron microscope is presented in Fig. 1. The examined steel was characterised by austenitic microstructure with numerous annealing twins and numerous primary precipitates of different size arranged inside grains. The twin formation is characteristic of face-centered cubic (FCC) metals and their alloys, and also austenitic steels that have low stacking fault energies and are subject to solution treatment after plastic deformation process. In the as-received condition of the examined steel, there may be MX [NbCrN and Nb (C, N)] and M$_{23}$C$_6$ (M$_5$Fe, Cr and Ni) precipitates [23] The identification of precipitates carried out with the transmission electron microscope revealed the existence of primary NbCrN and NbN precipitates in the examined steel, occurring in the last phase of solidification [24], which is shown in Figs. 2 and 3, respectively. The austenite grain size in HR3C steel was 4 according to the graphic pattern scale in [25].

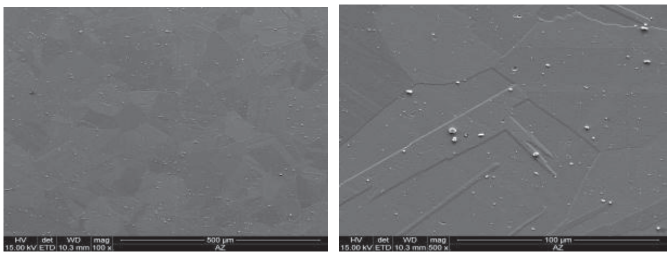


Fig. 1. Microstructure of HR3C steel in the as-received condition, hardness 179 HV10

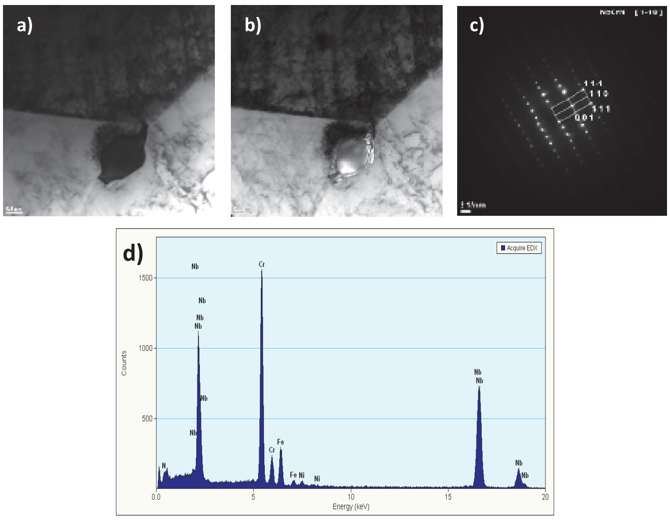
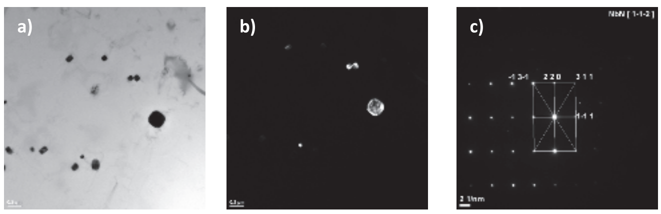


Fig. 2. Microstructure observed with TEM in HR3C steel in the as-received condition: a) bright field, b) dark field, c) diffractogram of NbCrN phase, d) EDS spectrum for NbCrN phase.



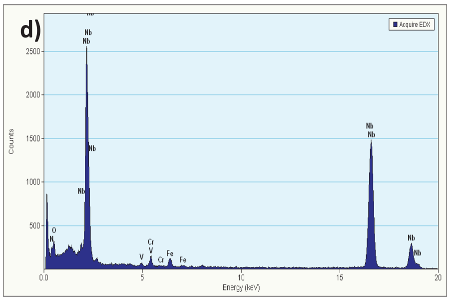


Fig. 3. Microstructure observed with TEM in HR3C steel in the as-received condition: a) bright field, b) dark field, c) diffractogram of NbN phase, d) EDS spectrum for NbN phase

The images of microstructure observed with the scanning electron microscope, revealing changes in HR3C steel after ageing at 650, 700 and 700 °C for 1,000 and 5,000 h, are presented in Figs. 4, 5 and 6, respectively.

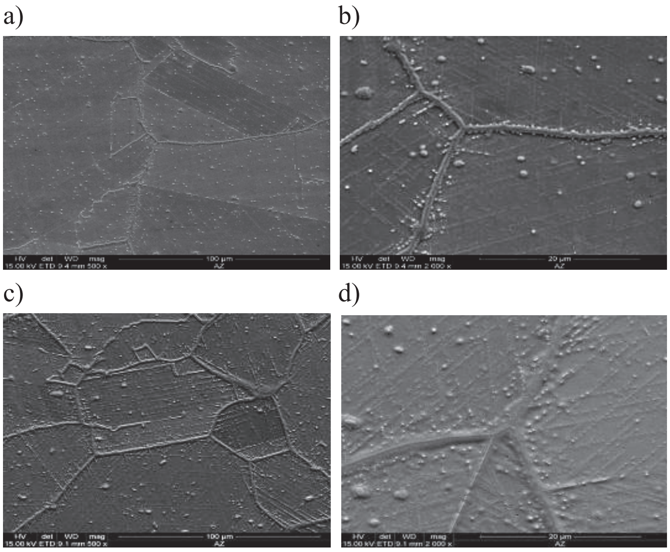


Fig. 4. Images of microstructure of HR3C steel after ageing at 650 °C a, b) 1,000h – hardness 186 HV10; c, d) 5,000 h – hardness 191 HV10

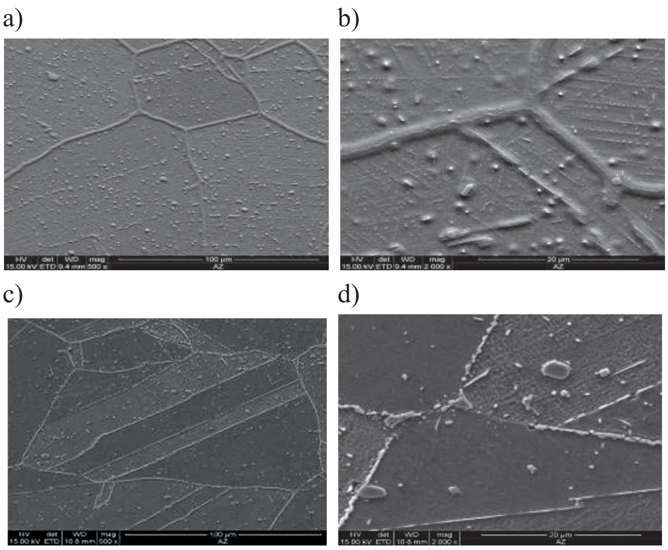


Fig. 5. Images of microstructure of HR3C steel after ageing at 700 °C a, b) 1,000h – hardness 207 HV10; c, d) 5,000 h – hardness 212 HV10

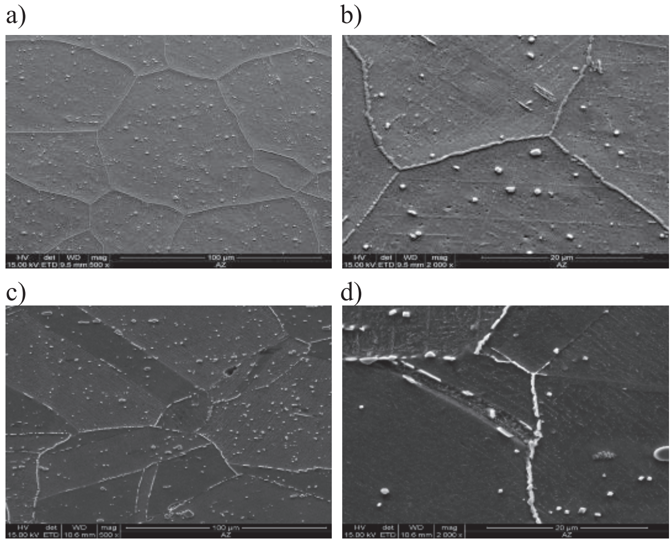


Fig. 6. Images of microstructure of HR3C steel after ageing at 750 °C a, b) 1,000h – hardness 214 HV10; c, d) 5,000 h – hardness 223 HV10

The changes in microstructure of austenitic-matrix steel due to long-term ageing at elevated temperature manifest themselves by secondary phase precipitation processes, preceded by chromium segregation in micro-areas adjacent to grain boundaries and followed by the formation of continuous, grid-like carbide arrangements. The example of surface distribution of chromium and iron for HR3C steel aged at 650 °C for 1000 h is shown in Fig. 7.

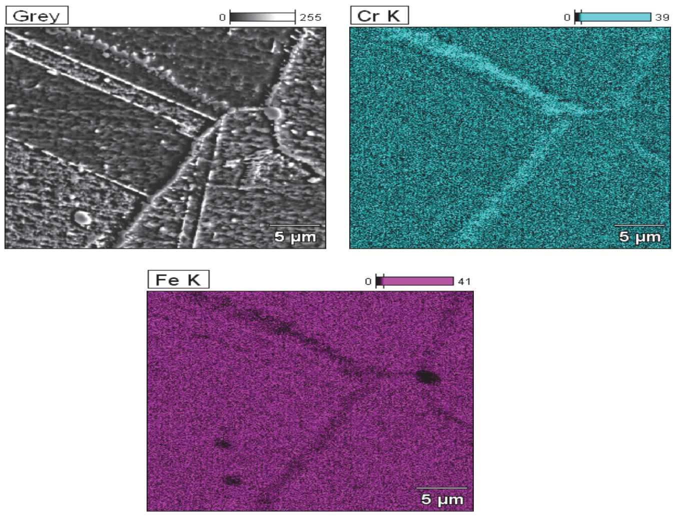


Fig. 7. Morphology of precipitates after ageing at 650 °C/1,000 h with surface distribution of chromium and iron

Ageing at 650 °C for 1,000 and 5,000 h resulted in precipitation and increase in the size of $Cr_{23}C_6$ carbides at the austenite grain boundaries, twins and sliding planes inside austenite grains with time (Fig. 4). The X-ray analysis of phase composition also revealed the existence of NbCrN and Cr_2N precipitates. These phases occur mainly inside grains, which is also confirmed in [26]. The average diameter of $Cr_{23}C_6$ precipitates was 198nm and 387nm after 1,000 and 5,000 h of ageing at 650 °C, respectively.

The intensification of the precipitation process in HR3C steel is noticed with increase in ageing temperature (Fig. 5).

This is confirmed by the measured size of $Cr_{23}C_6$ precipitates, which was 221 and 486 nm for ageing temperature of 700 °C and time of 1,000 and 5,000 h, respectively, whereas for ageing temperature of 750 °C the increase in average size of $Cr_{23}C_6$ precipitates with reference to temperature of 650 and 700 °C is rather significant and equals to 628 nm for the time of 1000 h and 945 nm for the time of 5,000 h (Fig. 6). Changes of similar nature in the size of precipitates in HR3C steel were observed in [27].

The phase composition of precipitates obtained by X-ray analysis of carbide isolates for the examined steel in the as-received condition and after ageing is summarised in Table 2.

TABLE 2

Results of phase analysis of HR3C steel isolates

Material condition	Phase composition
As-received condition	NbCrN – main phase
650 °C/1000 h	$Cr_{23}C_6$ – main phase, NbCrN, Cr2N, NbC
650 °C/5000 h	$Cr_{23}C_6$ – main phase, NbCrN, Cr2N
700 °C/1000 h	$Cr_{23}C_6$– main phase, NbCrN, Cr2N, NbC
700 °C/5000 h	$Cr_{23}C_6$ – main phase, NbCrN, Cr2N, NbC
750 °C/1000 h	$Cr_{23}C_6$– main phase, NbCrN, Cr2N
750 °C/5000 h	$Cr_{23}C_6$ – main phase, NbCrN, Cr2N

3.2. Strength properties

The ageing process conducted at a temperature to stimulate long-term service causes changes in microstructure affecting the strength and plastic properties of the material, which were assessed based on the results of static tensile test, hardness measurements and dynamic impact energy. The changes in mechanical properties of the HR3C steel depending on ageing parameters are presented in Figs. 8 and 9.

Ageing at 650 °C for 5,000 h had a significant impact on the increase in yield strength and tensile strength (Fig. 8). The value of yield strength (YS) after ageing was higher by 86 MPa, i.e. 25%, while the value of tensile strength (TS) was higher by 30 MPa – 4% compared to these properties in the as-received condition. After ageing at higher temperature – 700 °C, the values of these parameters maintain at a level higher by 18 and 6% for the yield strength and tensile strength, respectively, as compared to the as-received condition. After ageing at 750 °C for 5,000 h, the strength properties of the HR3C steel were similar to those in the as-received condition, and to be more precise, an insignificant decrease in tensile strength by 5% and increase in yield strength by 6% was found. For all the three ageing temperature levels within the time of 1,000 h, a sudden increase in the values of tensile strength and yield strength followed by their decrease with extension of the annealing time was observed, whereas the value of elongation (EI) after ageing at 650, 700 and 750 °C was being continually reduced as the ageing time was extended, and its decrease was the faster the higher ageing temperature was.

A similar course of changes in mechanical properties of the HR3C steel was observed in [24].

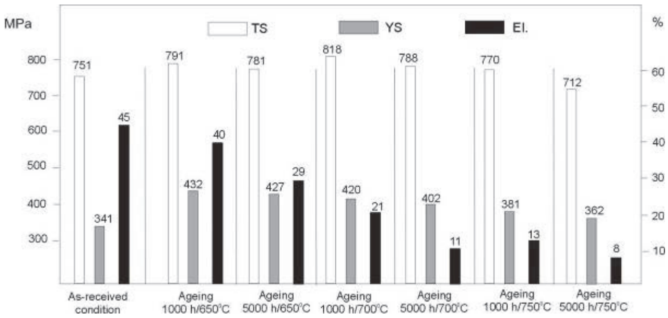


Fig. 8. Change in mechanical properties of HR3C steel during ageing at 650, 700 and 750 °C for 1,000 and 5,000 h

The ductile properties of the material were assessed based on the impact energy KV measurement on non-standard test pieces of 55x10x2.5 mm, which is the relative measure of impact strength the results of which are presented in Fig. 9. The trend in changes in KV impact strength reveals a similar course as the elongation (Fig. 8). Ageing for up to 1000 h results in a sudden decrease in impact strength from 108 J for the as-received condition to 32 J for the temperature of 650 °C, and then to 20 and 24 J for the temperature of 700 °C and 750 °C, respectively (Fig. 9). The extension of the annealing time is a continuous yet slow reduction in impact strength, with a tendency coincident with the change in elongation, with increase in the ageing temperature. The value of impact strength KV of the examined steel after ageing at 700 and 750 °C for 5,000 h is lower than the required minimum (KVmin = 27 J). The confirmation of low impact strength is the brittle nature of fracture observed already on test pieces aged at 650 °C/1,000h (Fig. 10)

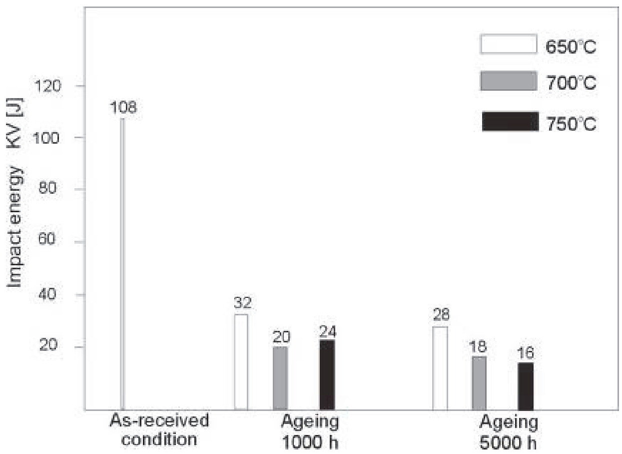


Fig. 9. Effect of time and temperature on impact strength of HR3C steel

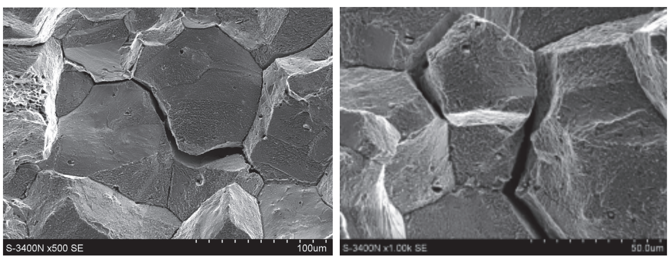


Fig. 10. Brittle intergranular fracture of impact test pieces from HR3C steel after ageing at 650 °C/1,000 h

4. Summary

Due to its high creep strength at elevated temperature and very good resistance to high-temperature corrosion and oxidation in steam provided by the formation of passivating chromium oxides Cr_3O_2, the HR3C steel is recommended for long-term service under creep conditions at up to 650-660 °C. The additional requirements for safe service of boiler structural components are defined in the Pressure Directive 97/23/EC, which, with regard to the properties of materials, refers also to meeting the specific ductility expressed by impact strength or impact energy with the minimum value of 27J, which is also considered as the relative measure of resistance to cracking.

The characteristics of high-temperature creep resisting materials that define their suitability for use at a specific temperature also include the results of investigations on microstructure stability and mechanical properties under laboratory annealing conditions at a temperature similar to that of the potential use. The ageing tests carried out at 650-750 °C for up to 5,000 h revealed the significant changes in microstructure consisting mainly in a tendency towards the formation of unfavourable morphology of mainly $Cr_{23}C_6$ carbides that form intermittent and continuous carbide arrangements at the grain and austenite twin boundaries (Figs. 4-6). These arrangements are already formed in the early stages of ageing at 650 °C for 500-1,000 h [23,27] when the thermally activated processes result in formation of chromium segregation in micro-areas adjacent to grain boundaries followed by the formation of continuous, grid-like carbide arrangements (Fig. 7). The coarse-grained austenite structure of HR3C steel in the as-received condition and the precipitation process at the grain and twin boundaries determine the unsatisfactory ductile properties expressed by the value of impact energy KV<27 J. The morphology of fractures after the impact test is characterised by explicit brittle nature of cracking (Fig. 10).

In the light of the above analysis, the need to continue the research and take a certain care when recommending HR3C steel to use for steam superheater pipes within the temperature range of approx. 650 °C can be formulated.

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