INFLUENCE OF DIFFERENT AUSTENITIZING TEMPERATURES AND HOLDING TIMES ON MICROSTRUCTURE AND SUBSTRUCTURE OF 9 CrNB CREEP RESISTANT STEEL

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Abstract

The paper deals with influence of four temperatures of high temperature austenitization and two dwells on temperature on microstructure and substructure of heat-resistant 9CrNB steel. The microstructure consists of lathe martensite and bainite. The presence of delta ferrite was demonstrated at specific austenitizing temperatures. Transmission electron microscopy showed that the substructure at all tested heat treatment was formed by martensite and bainite laths. They were identified as rod-shaped respectively needle-shaped particles based on extraction of laths into carbon replicas. Carbide particles M_3C-type were found by using diffraction analysis. Rod-shaped particles were excluded at the boundaries of the delta-ferrite grains, and these particles are MC type carbide particles according to the electron diffraction analysis. The presence of delta ferrite grains at the austenite grain boundaries effectively prevents their migration during austenitization and thus limits the growth of the mean austenite grain size in the austenitization temperature range of 1190 °C to 1230 °C. The presence of a larger amount of oval particles of the precipitate was identified at the austenitizing temperature of 1070 °C. It is very likely that they are NbC carbide particles according to the diffraction analysis. These particles should prevent a significant increase in austenite grain. This type of particles is observed only sporadically at a temperature of 1150 °C. The loss of the braking effect of NbC carbide particles on the migration of austenite grains caused the formation of significantly larger austenite grains at these austenitizing temperatures compared with the austenitizing state at 1070 °C.

Keywords: Austenitizing temperature, low carbon 9Cr creep resistant steel, grain growth, heat treatment

1. INTRODUCTION

Various martensitic 9-12 Cr steels are utilized currently in fossil fuel powered energy plants for their good elevated temperature properties such as creep strength, steam side oxidation resistance, fire side corrosion resistance, and thermal fatigue resistance. Need for further improvements on the properties of 9-12 Cr steels for higher temperature use is driven by the environmental concerns. Use of ultrasupercritical (USC) steam conditions in the new power plants is expected to achieve the increased efficiency. Several martensitic steels with 9-12 wt.% Cr content are being developed for the USC conditions in Japan and Europe [1]. Many studies have focused on increasing their high-temperature creep strength, e.g by optimizing the chemical composition. In service, these components of steel are subject to high-temperature cyclic loading (fatigue and creep). Creep resistance of steel is a result of the influence of microstructure, strength and plastic properties. The final heat treatment of these steels consists of high temperature austenitizing at 1150 °C - 1200 °C and subsequent tempering at a temperature range from 770 to 800 °C [2-6]. The aim of this work was to analyze the influence of various austenitizing temperatures and holding times on the microstructure and substructure of 9CrNB creep resistant steel.

2. MATERIAL AND EXPERIMENTAL METHODS

As the experimental material were used samples from low-carbon 9CrNB creep resistant steel, that have been heat treated (austenitizing) at the temperatures of 1070 °C, 1150 °C, 1190 °C and 1230 °C with holding time

30 a 120 min. The chemical composition of 9CrNB steel is shown in **Table 1**. The samples were prepared by standard metallographic procedures (grinding, polishing, and etching). Microstructural analysis was carried out using an Olympus GX51 light optical microscope. The state of precipitation of carbide and other phases in steel was analyzed by the JEOL JEM 2000FX Transmission Electron Microscope (TEM) by the method of carbon extraction replicas. They were after being separated in the Villela etchant removed from the metallographically prepared areas. The role of the analysis was to characterize the morphology of the transformed substructure, morphology, size and distribution of the precipitate particles.

Table 1 Chemical composition of 9CrNB steel

Elements	C	Mn	Si	P	S	Cr	Ni	Mo	W	Co	B	N
Min [wt. %]	0.06	0.40	0.20	-	-	8.00	-	-	2.50	2.80	0.010	0.005
Max [wt. %]	0.10	0.50	0.35	0.020	0.008	9.00	0.15	0.10	3.00	3.20	0.015	0.015

3. RESULTS

Austenitizing temperature 1070 °C (holding time 30 and 120 min, air cooling)

The microstructure in the conditions after austenitizing at temperature 1070 °C was formed by martensite and bainite. Microstructure was homogeneous from point of view of austenitic grain size. An average austenitic grain size was 38.1 μm at holding time 30 min and 43.1 μm at holding time 120 min. By evaluating the two conditions (30 min and 120 min) by TEM, by the methods of carbon replikas, it was found, that substructure was formed of martensite and bainite laths, which were created in relatively coarse original austenitic grains. Martensite and bainite laths are equally distributed and they have different orientation in different regions of the substructure. In the substructure, the original boundaries of austenitic grains were also observable on which the oval particles of precipitates were locally excluded.

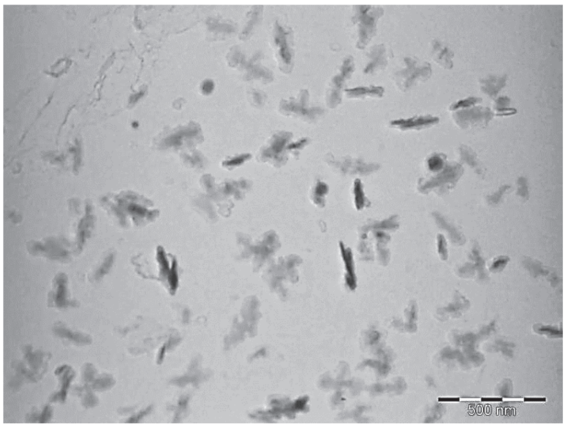

Figure 1 Detail of the particles in the bainitic lath, carbon replika, 1070 °C, 30 min.

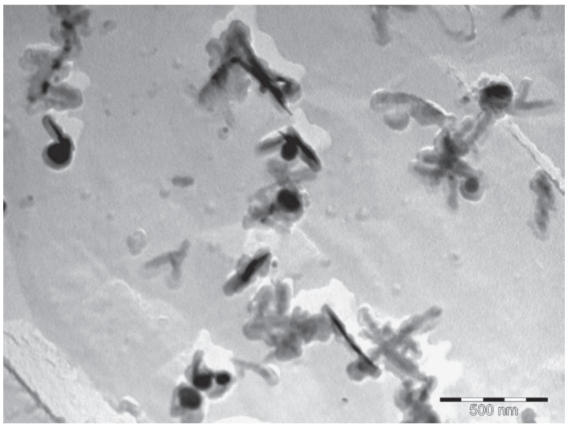

Figure 2 Detail of the particles in the bainitic lath, carbon replika, 1070 °C, 120 min.

These particles were often arranged in the substructure in rows that had only a partial relationship with the original austenitic grain boundaries. They reached a size of 300 nm. A small amount of smaller (size up to 100 nm) oval particles of precipitates was found inside the bainite and martensite laths and on their interfaces. The largest number achieved rod-shaped particles of precipitate located inside of bainite laths (**Figure 1, 2**). These particles, which are usually excluded in certain crystallographic planes of bainite laths, reached a length up to 200 nm. Diffraction analysis of the oval particle leads to the conclusion, that in the case of particles of this type, it is the MC carbide particles, most likely NbC. The greatest multiplicity reached the rod-shaped particles of precipitate, found inside the bainite laths. By diffraction analysis of rod-shaped particles it was found, that they are M_3C-type of carbides, in which M is most likely Fe. They are therefore cementite particles.

Austenitizing temperature 1150 °C (holding time 30 and 120 min, air cooling)

The microstructure in the conditions after austenitizing at temperature 1150 °C and holding time 30 and 120 min was formed by martensite and bainite. As can be seen, in comparison with the temperature of 1070 °C, there was an increase in austenitic grains size. At the holding time 30 min there was microstructure relatively homogeneous. The average size reached 105.5 μm. At the higher holding time 120 min was rarely observed heterogeneity in grain size. The average size reached 138.6 μm. The substructure of this state has many morphological features similar to the substructure of state annealed at a lower temperature. In the substructure, the boundaries of the original austenite grains (**Figure 3**) are visible, on which sporadically and individually were found oval or rod-shaped particles of size up to 50 nm. Larger multiplicity reached rod-shaped resp. needle-like particles of precipitate, located within the bainite laths. These particles, reached a maximum length of 700 nm and they are generally excluded in certain crystallographic planes of bainite laths. Their number is much smaller in comparison to the condition of 1070 °C/30 min. Substructure of heat treatment conditions of 1150 °C/120 min is very similar, such as at lower temperature (**Figure 4**). A small amount of oval particles of precipitates, reached a maximum size of 100 nm, rod-shaped particles reached a length of up to 300 nm.

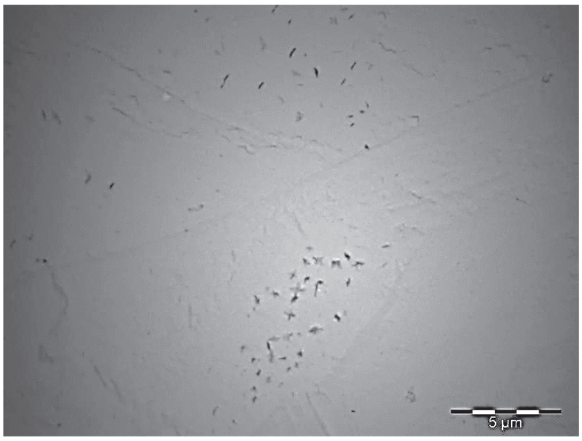

Figure 3 Substructure and distribution of the precipitates, 1150 °C, 30 min

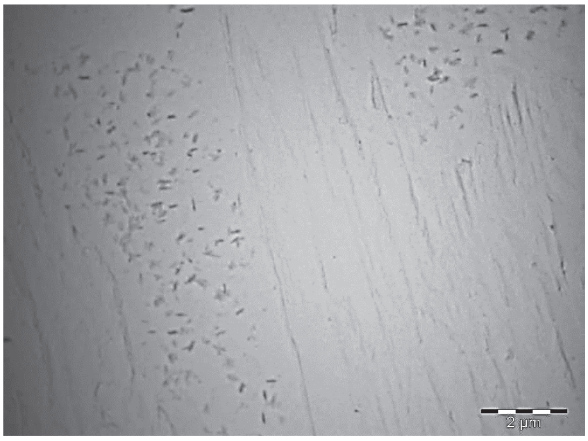

Figure 4 Substructure and distribution of the precipitates, 1150 °C, 120 min

Austenitizing temperature 1190 °C (holding time 30 and 120 min, air cooling)

The microstructure in the conditions after austenitizing at temperature of 1190 °C was formed by martensite, bainite and delta ferrite (3 %). Due to the presence of delta ferrite at the austenite grain boundaries, practically there was no increase in austenitic grain size compared to the grain size at the 1150 °C. At the holding time 30 min was microstructure relatively homogeneous. The average grain size reached 112.7 μm. At the holding time 120 min was microstructure slightly heterogeneous, the average grain size reached 139.8 μm. Substructure of this state, form bundles of martensitic and bainitic laths of different orientations, which have been formed in relatively large austenite grains. On the boundaries of the former austenite grains, often at the places of the triple points of the grain boundaries, there were delta-ferrite grains (**Figure 5**). On the grain boundaries of delta ferrite, rod-shaped particles were present (**Figure 6**), which according to the selective diffraction analysis are MC-type carbides, where M is likely V. These are carbides VC, resp. V_4C_3. In the areas of the former grain boundaries, particles were observed only rarely. Smaller quantities of oval particles, up to 100 nm, were found at the interface of bainite and martensite laths. Oval alternatively rectangular particles of maximum size up to 100 nm, excluded in small amounts, were also found inside the bainitic laths. Inside the bainitic baths predominantly rod-like (resp. needle like) particles whose length reached values up to 300 nm.

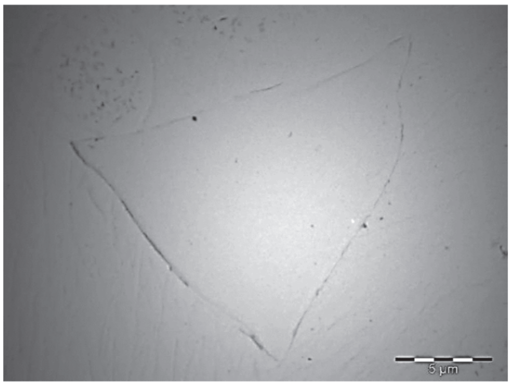

Figure 5 Delta-ferrite grain with particles at the boundaries, 1190 °C, 30 min.

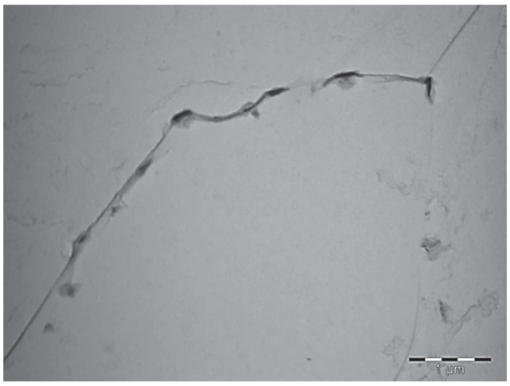

Figure 6 A detailed image of the particles present at the delta-ferrite boundaries, 1190 °C, 120 min.

Austenitizing temperature 1230 °C (holding time 30 and 120 min, air cooling)

The microstructure at austenitizing temperature of 1230 °C was formed by martensite, bainite and delta ferrite (5.5 %). At this temperature, the largest occurrence of delta ferrite was observed in the microstructure, which was excluded at the austenitic grains boundaries. As can be seen, the delta ferrite formations were the largest at this austenitic temperature (**Figures 7, 8**). Due to this excluded delta ferrite, decreased the size of the austenitic grains, the microstructure was finer than at temperature 1150 °C and 1190 °C. At the holding time 30 min the microstructure was relatively homogeneous. The average grain size was 114.5 µm. Also at the holding time 120 min the microstructure was relatively homogeneous. The average grain size was 99.2 µm. By analyzing the substructure of this state it has been found, that the structure is largely composed of martensitic and bainitic laths of different orientation, or bainitic formations in the shape of grains. These were formed in austenite grains with a relatively large average size. At the original boundaries of these grains, particles of precipitates were found rarely. In the areas of the former austenite grains, delta-ferrite grains were locally located. At martensite and bainitic laths, there was small amount of oval, resp. square particles of precipitates with a maximum size of up to 100 nm. There was also small amount of oval particles inside the bainitic laths, however, the rod-like (needles) particles, whose length reached values up to 300 nm. Rod-like resp. rectangular particles (sizes up to 250 nm) were also observed at the delta-ferrite grain boundaries. At the holding time 120 min in bainitic laths rod-shaped particles with a length of up to 400 nm predominated. In the substructure of the analyzed state, in all structural components also locally occur clusters of angular particles. By diffraction analysis of these particles, it was confirmed, that they were neither carbide nor nitride particles. At the delta-ferrite grain boundary, rod-shaped particles of size up to 400 nm were present. According to the diffraction analysis, these are MC carbide particles in which M is probably V.

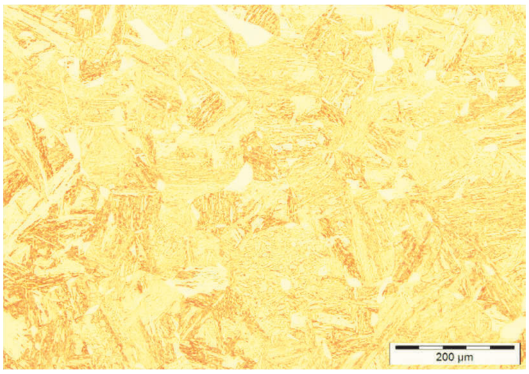

Figure 7 Microstructure at austenitizing temperature 1230 °C (martensite, bainite + delta ferrite), holding time 30 min.

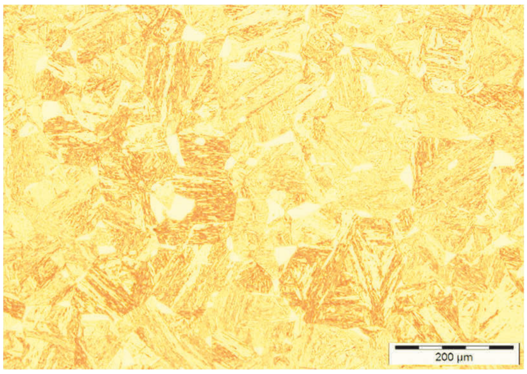

Figure 8 Microstructure at austenitizing temperature 1230 °C (martensite, bainite + delta ferrite), holding time 120 min.

4. DISCUSSION

The main objective of this work, as already mentioned in the introduction, was to analyze the influence of four austenitizing temperatures and two holding times on the microstructure and substructure of 9CrNB creep resistant steel, characterize the morphology, size of precipitates, and particle distribution of the precipitates. From the comparison of microstructural and substructural analyzes, it can be concluded that, no significant differences were observed when comparing 30 and 120 min holding time at one temperature. Larger differences in microstructures and substructures were observed, when comparing different austenitizing temperatures. From the view of the kinetics of austenitic grain growth can be concluded, that increasing the austenitizing temperature leads to increase of austenite grains size. But this applies only until the austenitizing temperature of 1150 °C. At higher temperatures of 1190 °C and 1230 °C the grain growth already did not occur, even occurred decreased of grain size. The reason was probably the presence of delta ferrite in the microstructure, which was excluded mainly on the grain boundaries. Due to this excluded delta ferrite (3 - 5.5 %) the grain growth was reduced and this possibly caused refinement of austenite grain size. Delta ferrite is according to the binary equilibrium diagram of Fe - Fe_3C stable at high temperatures (above 1396 °C). At the certain ratio of austenite forming and ferrite forming elements are this high temperature phase becomes stable at ambient temperatures. At the small content (over 5 %) may negatively affect the mechanical properties of steel [7]. 9 CrNB steel is the creep resistant steel alloyed mainly with Cr, W, Co and with optimal ratio of B / N [8, 9]. According to the authors of the work [10] the delta ferrite starts to equilibrate in the temperature of 1280 °C. However in microscale and the grain boundaries, where can be local enrichment (segregation) of ferrite forming elements, may result in the formation of delta ferrite at lower temperatures and to remain stable in non-equilibrium in the microstructure after cooling. Transmission electron microscopy showed that, in addition to martensitic laths, bainitic laths were also observed in the substructure. These were generally greater width and predominantly rod-like particles in them were observed. By diffraction analysis it has been shown, that it is a cementite Fe_3C. The rod-shaped particles were also observed at the delta ferrite grains. Probably these were VC particles. At the lowest austenitizing temperature of 1070 °C were observed in the substructure in a larger amount of oval particles. These particles were identified as NbC. At the temperatures (1150 °C and 1190 °C) particles of this type were observed only sporadically. These particles prevent significant growth of austenite grains. Loss of the braking effect of NbC carbide particles on the migration of austenite grains boundaries caused, that at these austenitizing temperatures, the formation of significantly larger austenite grains than, as in a state at the austenitization temperature of 1070 °C. Occurred to increase their size, especially in the states at 1150 °C and 1190 °C.

5. CONCLUSION

From the analysis of the influence of the various austenitic temperatures and the holding times on the microstructure and the substructure of 9CrNB steel the following conclusions:

1) The microstructure in the conditions after austenitizing was formed by lath martensite and bainite. At higher austenitizing temperatures (1190°C, 1230°C), the delta ferrite was also observed in the microstructure. The amount of delta ferrite with increasing the temperature grew (3 - 5.5 %).
2) From the comparison of microstructural and substructural analyzes, it can be concluded that, no significant differences were observed when comparing 30 and 120 min holding time at one temperature. Larger differences in microstructures and substructures were observed, when comparing different austenitizing temperatures.
3) Transmission electron microscopy (extraction replicas) showed that, in addition to martensitic laths, bainitic laths were also observed in the substructure. Delta ferrite was observed from temperature of 1190 °C. Cementite particles were observed in bainitic laths. At the grain boundaries of delta-ferrite rod-shaped particles were excluded, probably VC or V_4C_3.

4) At the austenitizing temperature of 1070 °C were observed in the substructure in a larger amount of oval particles. These are NbC carbide particles. These particles prevent significant growth of austenite grains. Their rare occurrence at higher temperature of 1150 °C caused an increase of grain size. The presence of delta ferrite grains at the austenite grain boundaries limits growth of the average size of the austenite grains at higher temperatures (1190 °C, 1230 °C).

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