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# Quantitative characterisation of the microstructure high chromium steel with boron for advanced steam power plants

**A. Zielińska-Lipiec*, T. Kozieł, A. Czyrska-Filemonowicz**
AGH University of Science and Technology,
Al. A. Mickiewicza 30, PL-30059 Kraków, Poland
* Corresponding author: E-mail address: alipiec@agh.edu.pl

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**Materials**

## ABSTRACT

**Purpose:** The purpose of the paper is to characterize the microstructure of high chromium steel with boron for advanced steam power plants.

**Design/methodology/approach:** The microstructure of new 12% chromium steel developed for advanced power stations operated around 625-650 °C, has been characterized in order to correlate its structural parameters with steel creep properties. Microstructure of the as received condition has a significant influence on creep resistance of 9-12% Cr steels operating at elevated temperatures. Quantitative TEM analyses of steel microstructure were undertaken to determine the dislocation density within the sub-grain, the width of the martensite laths/sub-grains and the particle parameters (shape, size, distribution). Phase identification was performed using electron diffraction and X-ray spectrometry. The influence of the austenitisation temperature (1060 -1100 ºC) on the microstructure of the VM12 steel with 145ppm boron was investigated.

**Findings:** The results show that increase of the austenisation temperature caused slight increasing of a sub-grain size and decreasing of dislocation density within sub-grains in the steel tempered at 780 ºC. The M23C6 and MX particle size was not significantly changed. Quantitative TEM analyses of the VM12 steel microstructure showed that favorable characteristics exhibit the steel which was austenised at 1060 °C.

**Research limitations/implications:** The present study is focused on the influence of temperature of autenitisation on the microstructure of the VM12 steel with 145ppm boron. The quantitative parameters of the VM12 microstructure were determined. The VM12 steel is a high Cr martensitic steel developed for advanced coal-fired power station operating at temperature higher than 600 ºC.

**Originality/value:** Quantitative characterisation of the microstructure high chromium steel with boron for advanced steam power plants.

**Keywords:** VM12 steel; Boron; Microstructure; TEM

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## 1. Introduction

Modifications of a chemical composition of the 9-12% Cr steels in recent 20 years created a hope of their use even in ultra supercritical conditions (USC). Addition of tungsten, molybdenum, vanadium and niobium affect the creep properties by solid solution- and precipitation hardening. Very important influence on the creep strength of high chromium steels has an addition of boron [1-7]. It was reported that time to rupture is significantly increased with increasing boron content in these steels. The high thermal resistance of the martensitic steels is related to small, resistant to growth sub-grains as well as to a presence of dispersed precipitates, mainly M(C,N) and $M_{23}C_6$, stabilizing the dislocation substructure.

Creep deformation of the high chromium martensitic steels during service exposure at high temperature is controlled by recovery process of the tempered martensite and strongly depends on the microstructure, especially dislocations substructure, phases precipitated within the sub-grains and on their boundaries. The microstructure of the as received steels, determined by their chemical composition and heat treatment conditions, influences creep resistance of these steels. Austenitisation temperature affects not only the prior austenite grain size and thus the morphology of martensite, but also the partial dissolution of number of elements in the martensite.

The present study is focused on the influence of temperature of autenitisation on the microstructure of the VM12 steel with 145ppm boron. The quantitative parameters of the VM12 microstructure were determined. The VM12 steel is a high Cr martensitic steel developed for advanced coal-fired power station operating at temperature higher than 600 ºC.

## 2. Experimental details

The VM12 steel of the chemical composition (in wt %) as 0.15C, 11.2Cr, 2.0W, 0.5Mo, 0.05 Nb, 0.27V and 145ppm B was delivered by Vallourec & Mannesmann Tubes for investigations performed within COST Action 536.

The specimens were heat treated by normalization (austenitisation) at two different temperatures 1060 °C and 1100°C for 30 min. and air cooled, followed by tempering at 780 °C for 2h, in order to obtain a martensite microstructure.

The microstructure of the as received steel was investigated using light microscopy (LM) and transmission electron microscopy (TEM). Thin foils were used for statistical determination of sub-grain for measurement of a dislocation density and for phase identification. The dislocation density within the sub-grains was measured using linear intersection method described by Ham [8]. Equivalent circle diameters for $M_{23}C_6$ particles (ECD = , where: A – particle area) were calculated using AnalySIS 3.1 computer programme. Experimental details are given in Ref. [9, 10].

## 3. Results and discussion

Light microscopy results indicated that the as received VM12 steel had fully tempered martensite microstructure. The effect of variations in austenitisation temperature on its microstructure is shown in Fig 1. Investigation of the effect of austenitisation temperature on the VM12 steel microstructure showed, that increasing temperature from 1060 to 1100 °C led to very fast increase of the prior austenite grain size from about 35 to 86 µm (Figs 1a, b).

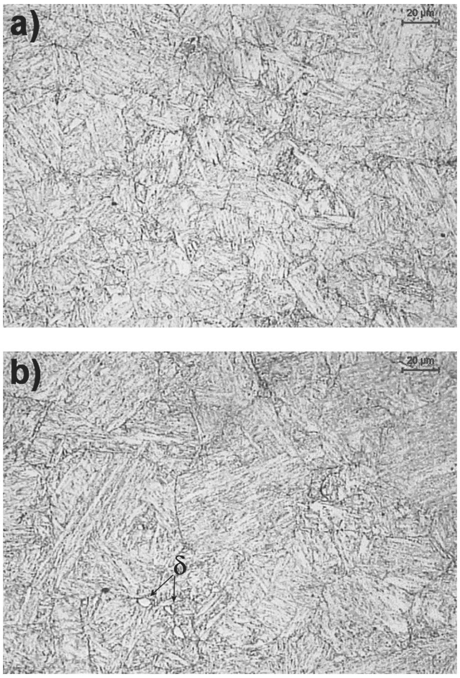


Fig. 1. Microstructure of the VM12 steel after austenitisation at a) 1060 °C, b) 1100 °C as seen by LM

Increasing of austenitisation temperature reduced the microsegregation, but it had an influence on the formation of δ-ferrite. Small amount of δ-ferrite was observed after steel austenitisation of at 1100 °C.

TEM investigation of tempered VM12 steel showed that its microstructure consists of tempered martensite. Typical microstructures observed after austenitisation and tempering are presented in Figs 2,3. The microstructure is dominated by elongated sub-grains with high dislocations density within the sub-grains. The $M_{23}C_6$ precipitated preferentially on prior austenite grain and sub-grain boundaries were observed. Within sub-grains the MX carbonitrides and carbides were precipitated on the dislocations. The precipitates of the MX type are important for steel mechanical properties. We observed spheroidal Nb-rich carbonitrides, the plate- like V-rich nitrides and complex ”V-wings” (NbC – VN), as shown in Fig. 4. The large, spheroidal particles Nb(C,N) remained un-dissolved during austenitisation and therefore inhibited the grain growth. During tempering they acted as the nucleation sites for plate-like V –rich nitrides, thus forming so-called “V-wing” complexes.

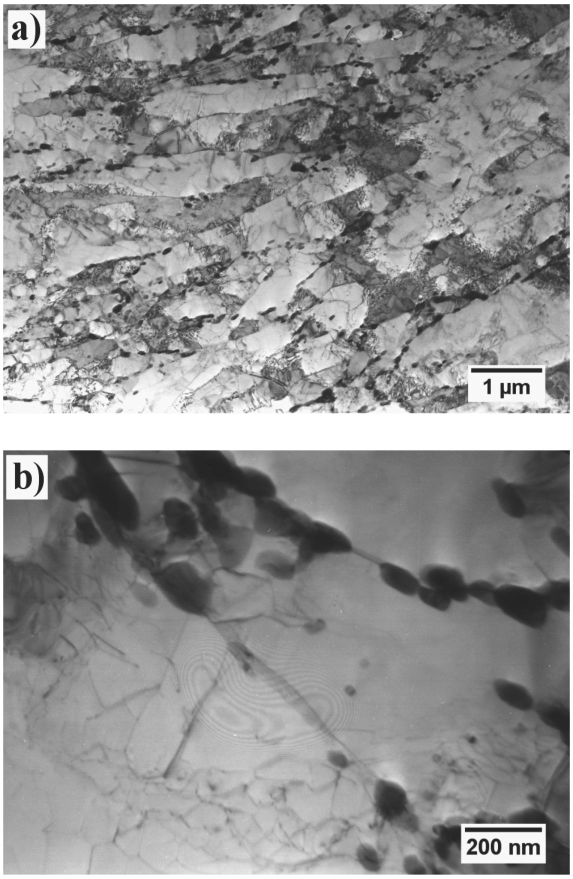


Fig. 2. TEM micrographs of the VM12 steel austenitised at 1060 °C: a) sub-grains and $M_{23}C_6$ precipitates, b) MX precipitates

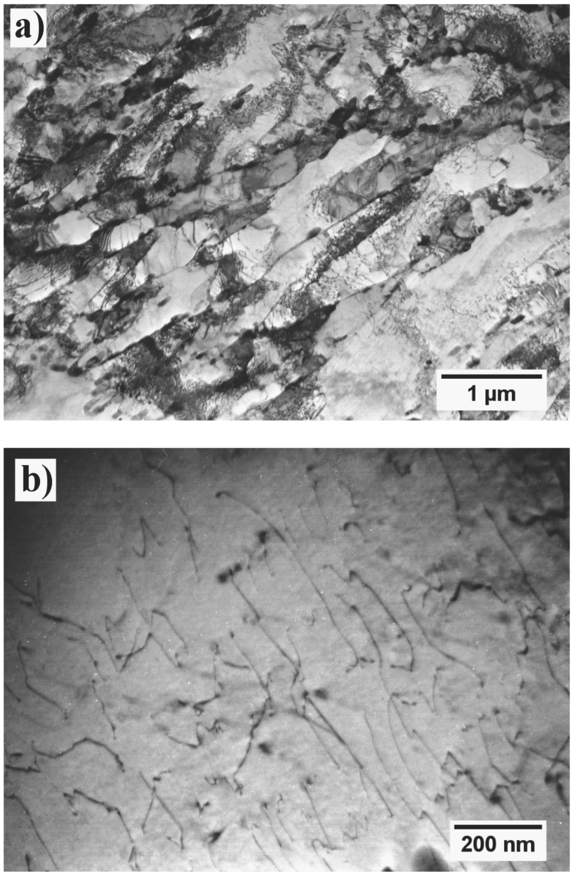


Fig. 3. TEM micrographs of the VM12 steel austenitised at 1100 °C: a) sub-grains and $M_{23}C_6$ precipitates, b) MX precipitates

Statistical quantitative analyses of the steel microstructure based on TEM micrographs, included determination of dislocation density within the sub-grains, the width of tempered martensite sub-grains and the precipitates parameters, permit to demonstrate differences in the microstructures after different austenitisation temperature. The results of the measurement of these parameters are given in Table 1 and Figs 5-6.

Table 1.
Microstructure parameters of the VM12 steel austenitised at 1060 and 1100 °C

| $T_{aust.}$ [°C] | Mean sub-grain ECD* [µm] | Sub-grain shape coefficient | Mean $M_{23}C_6$ carbides ECD* [nm] | Mean dislocation density [$m^{-2}$] |
|---|---|---|---|---|
| 1060 | 0.62 ± 0.26 | 0.56 | 87.8± 31.6 | $4.24\cdot10^{14}$ ± $0.93\cdot10^{14}$ |
| 1100 | 0.64 ± 0.19 | 0.46 | 88.6 ± 30.4 | $3.53\cdot10^{14}$ ± $1.78\cdot10^{14}$ |

Increase of the austenisation temperature caused a slight increasing of the sub-grain size, measured as the mean equivalent circle diameter (ECD). For the steel austenised at 1060 °C, max. ECD of the sub-grains was measured as 1.36 µm, but it was only 1.14 µm for steel austenised at 1100 °C. The relative frequency of 0.6 µm was higher in the steel austenised at 1100 °C in comparison with the steel austenised at lower temperature. Shape coefficient is lower for lower austenitisation temperature, what means that the sub-grains have more elongated shape in the steel austenised at lower temperature. The dislocation density within sub-grains decreased with increase of the austenisation temperature in the steel tempered at 780 ºC.

The $M_{23}C_6$ particle size and their shape were not significantly changed (shape coefficient of 0.81 for carbides in the steel austenised at 1060 °C and 0.83 for 1100 °C). The fine MX carbonitrides in the steel austenised at both temperatures were very similar and exhibit a diameter lower than 25 nm.

In the steels with elevated boron content an opposite phenomenon was found; large primary particles of $M_{23}(C,B)_6$ borocarbides were frequently observed as shown in the Fig. 4. The presence of such large particles results in reduced steel ductility and decrease the effectiveness of the impact of boron on the steel microstructure.

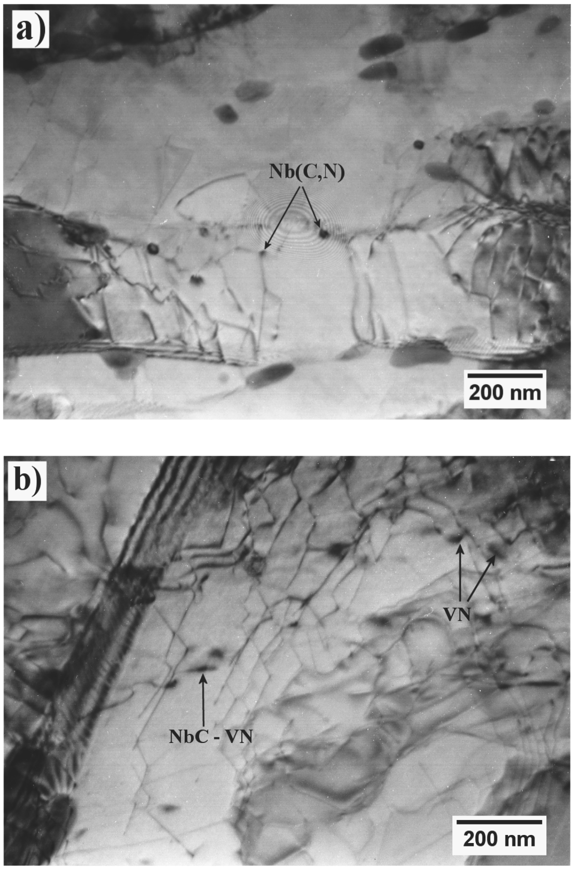


Fig. 4. MX precipitates observed in the VM12 steel

The stable $M_{23}(C,B)_6$ particles on grain and sub-grain boundaries, and/or martensite lath boundaries retard their growth by a pinning effect thus hindering the recovery processes not only during tempering but also during creep. The stabilization of the substructure by growth-resistant $M_{23}(C,B)_6$ borocarbides considerably improves the creep resistance of the steel. These results are in agreement with the result of the investigations of 9Cr-3W-3Co-VNb steel containing more than 100ppm B by Semba and Abe [2].

Further improvement of creep rupture strength of this high-boron steel is accomplished by the addition of appropriate amount of nitrogen enhancing MX precipitation.

Additionally, the lower growth rate of $M_{23}(C,B)_6$ borocarbides may prevent depletion of carbon in the matrix thus influencing favorably the precipitation of secondary MX particles. The dispersed particles preserve the high dislocation density to be retained during very long-term creep exposure.

## 4. Conclusions

The investigations of the influence of austenitisation temperature on the microstructure of VM12 steel with 145ppm of boron showed that increasing of the temperature from 1060 to

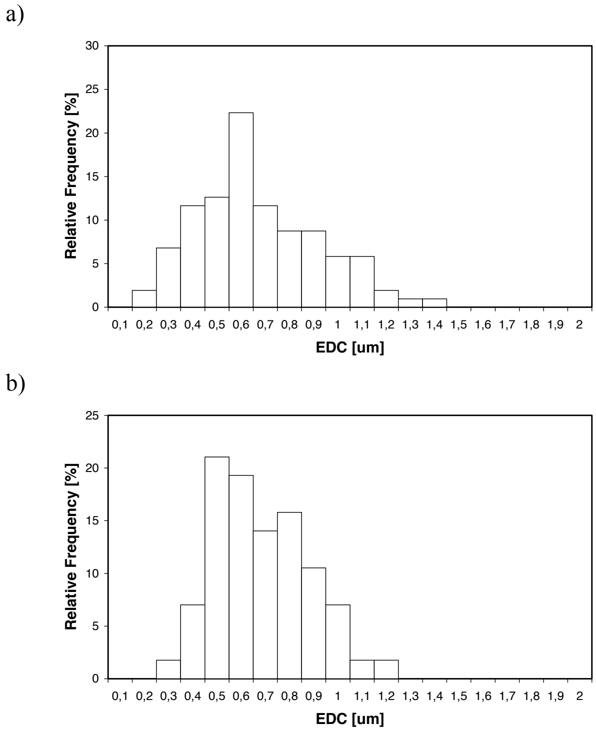


Fig. 5. Sub-grain size distribution in the specimen: a) austenitised at 1060 °C, b) austenitised at 1100 °C

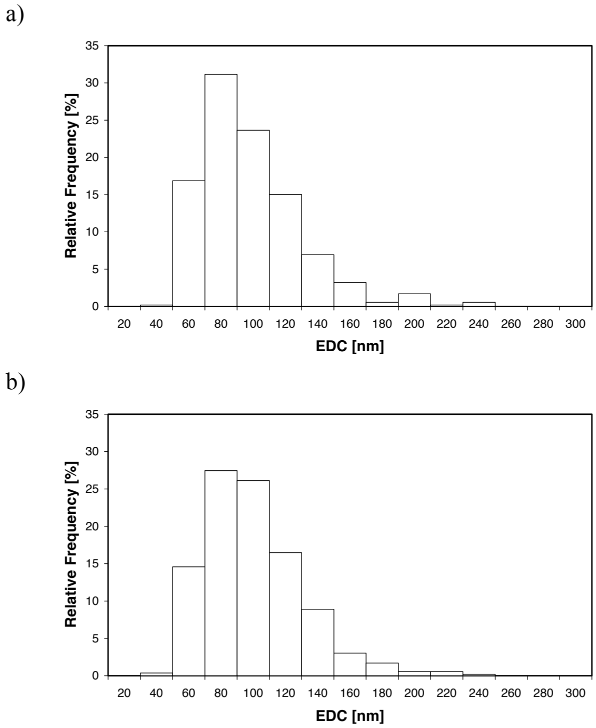


Fig. 6. Particle size distribution of $M_{23}C_6$ precipitates in the VM12: a) austenitised at 1060 °C, b) austenitised at 1100 °C

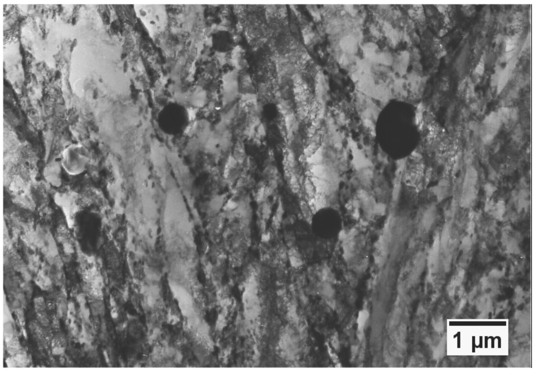


Fig. 7. Large primary particles of M23(C, B)6 borocarbides

1100 °C led to an increasing of prior austenite grain size, but also a volume fraction of delta-ferrite. After tempering, elongated sub-grains of tempered martensite were observed in prior austenite grains, the boundaries of which were decorated with $M_{23}C_6$ particles. Within the sub-grains, fine MX carbonitrides and carbides were precipitated on the dislocations. Increase of austenisation temperature caused slight increasing of a sub-grain size and decreasing of dislocation density within the sub-grains in the steel tempered at 780 ºC. The $M_{23}C_6$ and MX particle size was not significantly changed. In investigated heats, large (primary) particles of $M_{23}(C,B)_6$ was observed.

Quantitative TEM analyses of the VM12 steel microstructure showed that favorable characteristics exhibit the steel austenised at 1060 °C.

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