SEM, TEM and SLEEM (scanning low energy electron microscopy) of CB2 steel after creep testing

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Abstract. The demand to produce electrical power with higher efficiency and with lower environmental pollution is leading to the use of new advanced materials in the production of power plant equipment. To understand the processes taking place in parts produced from these materials during their operation under severe conditions (such as high temperature, high stress, and environmental corrosion) requires detailed evaluation of their substructure. It is usually necessary to use transmission electron microscopy (TEM). However, this method is very exacting and time-consuming. So there is an effort to use new scanning electron microscopy techniques instead of TEM. One of them is scanning low energy electron microscopy (SLEEM). This paper deals with an assessment of the possibility to use SLEEM for describing the substructure of creep resistant steel CB2 after long-term creep testing. In the SLEEM images more information is contained about the microstructure of the material in comparison with standard scanning electron microscopy. Study of materials using slow and very slow electrons opens the way to better understanding their microstructures.

1. Introduction

Turbines, boilers and steam piping are among the most exposed parts of steam power plants. They operate under severe service conditions for several decades. Therefore, high mechanical strength, good corrosion/oxidation resistance and high structural stability of the materials used for their production are desired. Several new grades developed on the basis of modified 9Cr-1Mo steels in the last few decades are currently used for the production of various parts of high efficiency power plants. Their chemical composition is balanced with the aim of improving oxidation and creep properties. Alloying with chromium increases the oxidation resistance, however its high content (higher than 9 %) causes precipitation of Z-phase, dissolution of fine MX precipitate and a decrease in long-term creep strength. Limitation of nickel content improves creep strength. Addition of cobalt compensates the low Ni content and restrains the formation of δ-ferrite. Nitrogen together with vanadium and niobium can increase precipitation strengthening and boron can restrict coarsening of chromium carbides that pin grain and sub-grain boundaries and causes an increase in sub-structural strengthening. A balanced content of molybdenum and tungsten increases solid solution strengthening and long-term structure stability. Precipitation of secondary phases during service may have an adverse effect on the mechanical properties such as tensile and creep strength, fatigue, etc. Cast steel CB2 developed in Europe is one of the most promising alloys for production of steam turbines working in
ultra-supercritical conditions [1]. The changes of substructure – precipitation and dissolution of precipitates, dislocation density – have to be observed using transmission electron microscopy (TEM). It is very labour intensive and time-consuming. Standard scanning electron microscopy (SEM) is inapplicable in many cases due its insufficient resolution for investigation of some structural features (e.g., fine precipitates). Thus, new methods of SEM are tested with the goal of improving observation capability.

Scanning low energy electron microscopy (SLEEM) is beneficial for the investigation of many different types of materials. This technique can be used for improving image parameters, such as atomic number and crystallographic contrast. The aim of this study is to analyze the microstructure of cast CB2 steel using ultra-high and standard high vacuum scanning electron microscopes equipped with cathode lens mode, which enables us to observe samples at arbitrary landing energy of primary electrons. In the SLEEM images more information is contained about the microstructure than with standard scanning electron microscopy (SEM). Study of materials using slow and very slow electrons open the way to better elucidation of their microstructures.

This paper deals with the possibility of using SLEEM for the study of advanced creep resistant steel COST CB2.

2. Experimental materials and methods

2.1. Experimental materials

Research and Testing Institute Plzeň Ltd. performed measurement of mechanical properties, long-term creep test to ruptures at a temperature of 650 °C, fractography analyses and a quantitative assessment of microstructure as a part of a collaborative effort in the framework of the COST 501 and 522 programmes. The tested samples were machined from the 5t pilot valve CB2P produced by PHB Stahlguss GmbH (Germany) with dimensions which corresponded to the real valve of the steam turbine. The heat treatment consisted of annealing at 1100 °C for 9 h, cooling with compressed air, annealing at 740 °C for 10 h and at 730 °C for 24 h. Mechanical and creep testing of the valve were carried out at three localities marked A, B and C showing the various wall thicknesses (130, 85 and 50 mm, respectively) [1]. Three of the creep tests are still running and the longest time to rupture at the time of publication is about 90,000 hours.

The microstructure of the virgin material and crept specimens (tested at 650 °C and stresses at 60 and 85 MPa) taken from locality B were investigated.

2.2. Experimental methods

The samples were studied at Research and Testing Institute Plzeň Ltd. using “standard” methods of SEM and TEM. Observation was performed using microscopes JEOL JSM 6490 LV, JEOL JEM 1200 EX, and a microanalyser INCA ENERGY 300. Carbon extraction replicas were prepared from electrolytic polished and etched metallographic samples. Thin foils were prepared using a jet electropolishing. Secondary phases were identified on the basis of EDS microanalysis and electron diffraction.

In addition evaluation of selected samples was performed at the Institute of Scientific Instruments of the Academy of Sciences of the Czech Republic. The microstructures of specimens were studied under standard vacuum in scanning electron microscope JEOL 6170F and in the ultra-high vacuum SEM (UHV SLEEM) of own design. UHV SLEEM consists of three separate vacuum chambers. One of them is the observation chamber equipped with a two-lens field emission electrostatic electron optical column (FEI Company) and CL system. The second chamber is intended for in-situ cleaning of the samples and incorporates an argon ion beam gun for surface cleaning. The third chamber is the loading chamber of the air lock. Both these microscopes are equipped with cathode lens (CL) mode which enables us to observe specimens at the arbitrary landing energy of primary electrons. The principle of the CL mode is shown in figure 1 and as you can see the cathode of the CL is formed by a negatively biased specimen and the anode of the CL is created by the detector based on the ground
potential. The primary beam is retarded in the field of the CL to the final landing energy and the electrons emitted from the specimen are collimated and accelerated towards the detector [2]. The information about crystallographic orientation was obtained using electron backscattered diffraction (EBSD) in a Philips XL30 SEM.

![Figure 1. Schematic sketch of the cathode lens.](image)

Observation of specimens using very slow electrons requires in-situ cleaning of the surface from native oxide layers. The native oxide is impenetrable for a low energy primary beam and its presence prevents observation of the real microstructure. This situation is demonstrated in figure 2, which shows the comparison between the in-situ cleaned and rough areas together with X-ray photoelectron spectroscopy (XPS). XPS analysis shows that the specimen surface is covered by Fe$_3$O$_4$, Fe$_2$O$_3$ and Cr$_2$O$_3$ oxides.

![Figure 2. Surface of CB2 steel: a) in-situ cleaned area; b) as-inserted oxidized area, together with the XPS spectra of the oxidized area.](image)
3. Results

3.1. Substructure assessment using standard SEM and TEM

The microstructure of the virgin CB2 sample corresponds to tempered martensite without δ-ferrite, with some evidence of dendritic segregation and shrinkage porosity. Aluminate inclusions and large BN precipitates up to 5 µm in size were observed in etched metallographic samples. They occurred close to the prior austenite grain boundaries, in regions where the boron content exceeded the limit of boron solubility in solid solution (figure 3). Thus the boron atoms bonded in primary nitrides cannot be active in the stabilisation of chromium carbides. A high density of relatively large chromium rich M23C6 carbides was found in the specimens before and after the creep tests. Their size did not exceed 0.5 µm (figure 3).

![Figure 3. Metallographic sample of virgin specimen etched in Villela-Bain's reagent. SEM micrograph.](image)

A lot of Laves phase particles were observed in the etched metallographic samples and also in the carbon extraction replicas (figure 4). These particles were concentrated around coarse BN precipitates or formed clusters with coarse NbN particles. Fine (V,Nb)N precipitates were observed in the replicas and were detected also in thin foils.

![Figure 4. Carbon extraction replica of virgin specimen. TEM micrograph.](image)
Various types of grain boundaries were evident in the structure of tempered martensite. High angle boundaries separated prior austenite grains, which consisted of blocks of martensite laths at different levels of recovery, which occurred during tempering and creep testing. Before creep tests blocks consisted of laths with relatively high dislocation density (in the order of \(10^{14} \text{ m}^{-2}\)) and laths divided by dislocation walls into sub-grains with significantly lower dislocation density (in the order of \(10^{13} \text{ m}^{-2}\)). Relatively coarse \(\text{M}_{23}\text{C}_6\) carbides and \(\text{Fe}_2\text{Mo}\) Laves phase pin dislocations at the sub-grain boundaries, fine \(\text{MX}\) nitrides pin slip dislocations within the sub-grains (figure 5).

![Figure 5. Thin foil of virgin specimen. TEM micrograph.](image)

Coarsening of Laves phase occurred during creep tests and new Laves phase particles nucleated on the site of \(\text{M}_{23}\text{C}_6\) carbides, \(\text{NbN}\) and \(\text{BN}\) nitrides. Significant growth of Laves phase occurred after creep exposure for 17,924 h and 13,962 h respectively. With regard to \(\text{M}_{23}\text{C}_6\) carbides, no important changes were found in their size and distribution. Density of fine \(\text{MX}\) nitride was higher than in as received conditions. After a creep test with the time to rupture of 67,857 h further coarsening of Laves phase was observed and a significant decrease in the density of fine precipitates. Some new plate-like particles containing \(\text{V}, \text{Cr}, \text{Nb}\) and \(\text{N}\) were observed in the carbon extraction replicas, which could correspond to undesirable the \(\text{Z}\)-phase.

### 3.2. Substructure assessment using advanced SEM

The atomic number and crystallographic contrast is caused mainly by backscattered (BSE) electrons (i.e., electrons that are leaving the sample with energy higher than 50 eV and by elastic scattering). The BSE leave the specimen surface at a wide range of angles relative to the optical axis. The electrons backscattered at low angles from the optical axis mainly carry information about chemical composition and electrons backscattered at high angles are sensitive to the density of atoms within the crystal lattice [3].

#### 3.2.1. Tuning of material contrast.

The low beam energy and thus the low penetration depth are necessary for observing small surface features, such as fine precipitates. A mean free path of inelastically scattered electrons decreases with decreasing landing energy of the primary electrons, which makes this method extremely surface sensitive. Figure 6 shows the UHV SLEEM images of the in-situ cleaned specimen acquired at conditions of the landing energies from 6017 eV (= primary beam energy) to 4 eV. The electrons were retarded by means of the negative bias applied on the specimen surface. The micrographs obtained from the same field of view demonstrate increasing crystallographic contrast with decreasing landing energy until 50 eV, where the minimum of the escape depth is reached [9]. At this landing energy the escape depth of electrons is the least and
thereby detected electrons are the least affected by the arrangement of atoms in the matrix, which finally causes a significant deprivation of crystallographic contrast. On the other hand, the fine precipitates located on the surface are visible.

Figure 6. a) Dependence of the escape depth on the kinetic energy of electrons [9]; together with the UHV SLEEM images of the same area acquired at: b) 4 eV, c) 50 eV, d) 500 eV, e) 3000 eV, and f) 6017 eV landing energy of electrons. All images were taken at the same image contrast.

Figure 7 shows images of a specimen cleaned in-situ obtained under ultra-high vacuum conditions (figures 7a and b) in the UHV SLEEM microscope, together with the image of the same area in a JEOL 6170F SEM (standard high vacuum, without in-situ cleaning). Figure 7 demonstrates that the small precipitates of Laves phase near shrinkage porosity are not visible in standard SEM and can be successfully imaged only in the CL mode. Figure 7d and the attached table show the results of ED microanalyses of Laves phase particles and matrix. Thus, using the CL mode it is possible to visualize areas with very small difference in chemical composition and this technique provides a powerful tool for examining multi-component materials.
Figure 7. The effect of beam energy and cleanliness of the specimen surface on material contrast. UHV SLEEM images obtained at a) 6017 eV, and b) at 10 eV (primary beam energy = 6017 eV). c) shows standard SEM image obtained at 5 keV landing energy of electrons; and d) attached table shows positions and results of EDS microanalysis in wt%.

3.2.2. Sensitivity to crystallographic orientation. Backscattering of electrons is the source of one of the most important image signals in SEM. In the CL mode of SEM a combination of secondary electrons with (slow) backscattered electrons (including electrons backscattered at high angles from the optical axis) is acquired, providing micrographs with high crystallographic contrast even under conditions available in a standard SEM. Figure 8 shows the UHV SLEEM images obtained from CB2 steel at 4 keV (a) and 1 keV (b) landing energy of electrons, together with the corresponding crystallographic orientation map obtained from the EBSD measurement (c) and with simulations of the BSE trajectories (d, e). Acquisition of the high angle electrons enables the contrast between martensite laths to be observed with extremely high contrast.

Figure 8. UHV SLEEM images obtained at a) 4 keV and b) 1 keV, together with c) EBSD map of the same area; and d, e) corresponding simulations of BSE trajectories in the electron optical design (EOD) software [6].
Evolution of the contrast between the individual martensitic laths is displayed in figure 9. The primary beam energy was fixed at 6019 eV and the landing energy was governed by means of electrostatic field formed by the cathode lens system. Series of the UHV SLEEM images shows the increasing contrast of martensitic laths with the increasing immersion ration (primary beam energy / landing energy ratio). Such high sensitivity to the structure details using the UHV SLEEM cannot be achieved using the standard SEM BSE image (figure 9z). At electron energies in the order of keV, the crystal orientation contrast is week due to the detection of the BSE scattered close to the optical axis, which carry the major information about the chemical composition. At lower energies, the electrons are collimated towards the optical axis and detection of the high angle BSE causes increasing crystallographic contrast [4, 5, 7, 8].

Figure 10 shows the graph of the image brightness variation across the line X-Y marked in figure 9o. The comparability of the images is guaranteed using of the same settings of image contrast during their acquisition. From this graph is evident that the best contrast between the laths of different orientation is obtained at 500 eV landing energy of primary electrons.

4. Conclusion

Scanning low energy electron microscopy is a promising new method for evaluating the microstructure of advanced creep resistant steels used in the power industry.

It is possible to assess local crystal structure or phase composition at high resolution in relation to the incident electron energy.

The main advantages of scanning low energy electron microscopy are the many opportunities for using the method not only in fundamental research but also in practice. This method offers the possibility of studying materials with an extremely high sensitivity to the crystallography and chemical composition. Knowledge of the crystallography and chemical composition of materials is important for a better understanding of their microstructures and provides a key for the development of materials with unique mechanical and physical properties.
Figure 9. The same area acquired at landing energies of: a) 0 eV (i.e., total reflection); b) 2 eV; c) 8 eV; d) 11 eV; e) 16 eV; f) 26 eV; g) 60 eV; h) 100 eV; ch) 150 eV; i) 200 eV; j) 250 eV; k) 300 eV; l) 350 eV; m) 400 eV; n) 450 eV; o) 500 eV; p) 1000 eV; q) 1500 eV; r) 2000 eV; s) 2500 eV; t) 3000 eV; u) 3500 eV; v) 4000 eV; w) 4500 eV; x), 5000 eV; y) 5500 eV; and z) 6019 eV.
Figure 10. A graph of the intensity variation across the martensitic structure along the line X-Y (in figure 9o).

Acknowledgements
We are very grateful for the financial support of our research from the project no. TE01020118 (Competence centre: Electron microscopy) from the Technology Agency of the Czech Republic.

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