Comprehensive TEM studies on Cr-rich martensitic steels

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Improved tempered martensitic 9-12 % Cr steels are currently developed in order to rise the energy efficiency of thermal power plants by increasing steam temperature and pressure [1-2]. However, in the long-term an unexpected drop in creep rupture strength has often been observed. The proposed mechanisms are mainly due to the progression of microstructural degradation during creep exposure. By adding boron in homeopathic amounts (~100 ppm) the creep rupture strength at long times was considerably improved.

Different secondary precipitates were characterized in TEM by using integrated spectroscopic techniques such as electron energy loss spectroscopy (EELS) and X-ray spectroscopy (EDXS). These data combined with energy filtered TEM, high resolution TEM and some off-line methods like bi- and tri-variate histogram analysis and near edge fine structure analysis of interstitial elements (B, C, N, O) may help understanding the nucleation and/or elemental enrichment of different phases.

All these methods have been used to identify different nitride phases like MN, M_2N and modified Z-phase. Modified Z-phase particles, formed at an early stage, having chromium rich cores with very thin vanadium rich shells, have been observed in the HRTEM investigation and proved by EELS line scans (see Fig. 1). Elemental quantification of EEL spectra [3] suggests that a transformation of both MN and M_2N into the modified Z-phase, despite of their different crystallographic structure and formation potentials [4], may be possible, if a diffusion of the nitrogen is accounted for.

The boron in very low concentration delays the coarsening of $M_{23}C_6$ carbides considering that the boron atoms occupy the vacancies in the vicinity of growing carbide interfaces near prior austenite grain boundaries. Analytical methods such as atom probe field ion microscopy [5] and scanning Auger spectroscopy [6] confirmed the presence of boron in such carbides.

The amount of boron in the $M_{23}C_6$ carbides, found in a 9Cr-3W-3Co-VNb steel containing 120 ppm of boron and 130 ppm of nitrogen [6], has been quantified by means of electron energy loss spectroscopy (EELS). To avoid the possible hydrocarbon contamination, the EEL spectra have been acquired in imaging modus (see Fig. 2). For intensity extraction we used the multiple linear least square fit (MLLS) method. We found that 2% of the carbon content was replaced by boron ($M_{23}C_{5.88}B_{0.12}$). This result is in very good agreement with scanning Auger spectroscopy measurements done by Abe [7].

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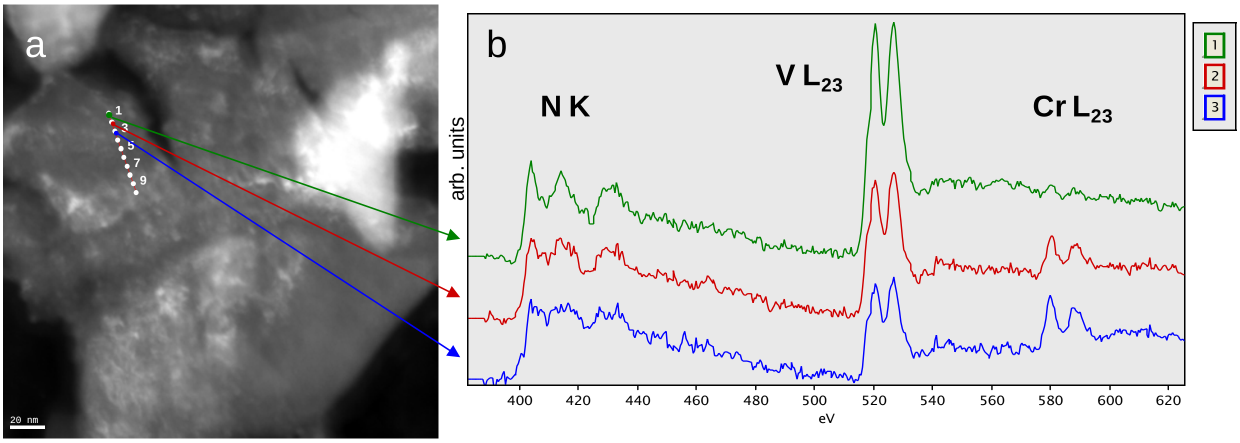

Figure 1. a) STEM HAADF picture of an early stage mod. Z-phase. b) EELS line scan taken with a beam of 0.36 nm diameter.

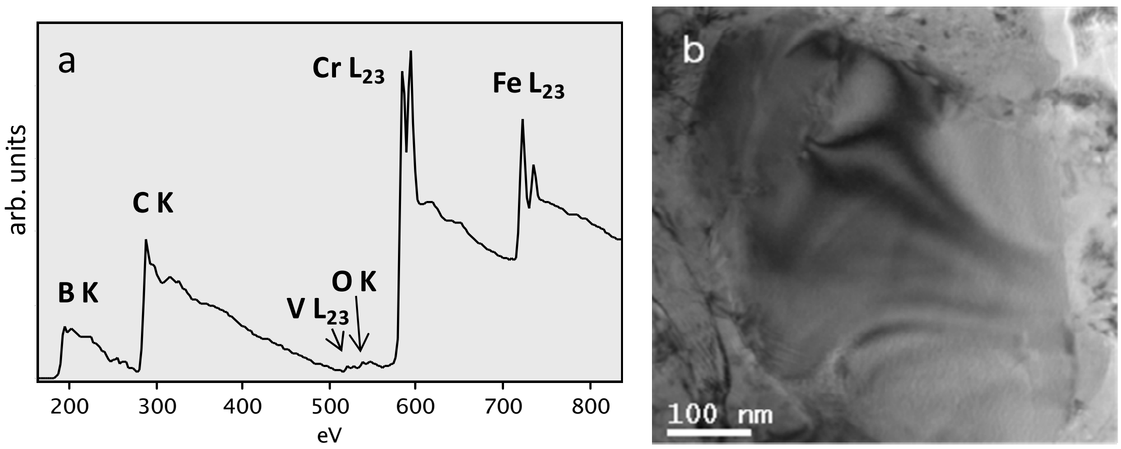

Figure 2. a) EELS from a $M_{23}(C, B)_6$ carbide, where 2 at.% of carbon is replaced by boron. b) Zero loss filtered image.

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