

## TEM study of secondary precipitates influencing creep strength of martensitic VM12 steel

A. Zielinska-Lipiec, T. Koziel, A. Czyrska-Filemonowicz,

AGH University of Science and Technology, Al. Mickiewicza 30, PL-30059 Kraków, Poland

alipiec@agh.edu.pl

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Martensitic VM12 chromium steel was recently developed for advanced coal-fired power stations which can operate reliably at high temperatures and pressures. Its creep resistance is dependent on a stability of its microstructure during long-term creep exposure. Destabilization of microstructure is caused by recovery and softening processes of a tempered martensite and strongly depends on changes of a dislocation substructure and morphology secondary particles during service exposure. Quantitative TEM analyses of VM12 steel were undertaken to determine the microstructure parameters in the as received- and long-term creep deformed steel at 625°C up to around 29 000h.

The microstructure of the VM12 steel was characterised by X-ray diffraction, light microscopy (LM), scanning (SEM) and analytical transmission electron microscopy (TEM). TEM investigations were performed on thin foils prepared by conventional jet polishing and double extraction replicas. Phase identification was done by electron diffraction (SAED) and STEM-EDS. The diffraction patterns were interpreted with the JEMS software [1]. LM and TEM image analyses were performed using AnalySIS programme.

Tempering of the VM12 steel (as received condition) at 780°C for 2h resulted in a high dislocation density ( $6.57 \pm 1.4^{14} \text{m}^{-2}$ ) and fine sub-grain microstructure ( $0.6 \pm 0.2 \mu\text{m}$ ), as seen on Fig. 1a. The  $\text{M}_{23}\text{C}_6$  carbides (mean diameter:  $110 \pm 36 \text{ nm}$ ) and MX carbonitrides (mean diameter:  $32 \pm 9 \text{ nm}$ ) were main strengthening particles of the steel. High temperature, long exposure time and stresses caused changes in VM12 steel microstructure during creep. Typical VM12 microstructure after creep deformation at 625°C for 28 983h is shown in Fig. 1b. Well developed sub-grains (size increased to  $1.4 \pm 0.2 \mu\text{m}$ ) with low dislocation density (decreased to  $1.2 \pm 0.8^{14} \text{m}^{-2}$ ) are characteristic microstructure features of long-term exposed specimens.

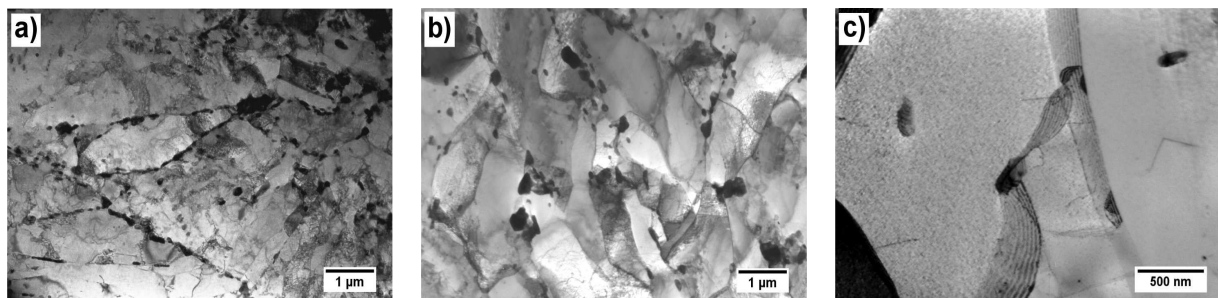
The size, morphology and distribution of precipitates have changed during creep deformation, what influenced creep strength. The  $\text{M}_{23}\text{C}_6$  carbides increased rapidly; their mean diameter is double larger after creep for about 15000 -17500 h, in comparison with as received condition. These particles are very important for stabilization of sub-grain microstructure during creep (Fig. 1c). Fine MX particles precipitated intergranally (Fig. 2a). During creep at 625°C, the mean diameter of MX particles first increased (until 3000 h of creep) to  $41 \pm 17 \text{ nm}$  and then slowly decreased with prolongation of creep duration ( $22 \pm 9 \text{ nm}$ ); simultaneously a density of MX carbonitrides decreased. It indicates that MX particles are thermodynamically unstable and during long-term exposure dissolved.

Further microstructural TEM investigations revealed precipitation of a complex Cr(V,Nb)N nitrides (Fig. 2b), called Z-phase [2]. Large Z-phase precipitates were found frequently in contact with VX precipitates, which might acted as nucleation sites for Z-phase (Fig. 2b) [3]. After creep during 15000 h, only very few particles was observed. The density

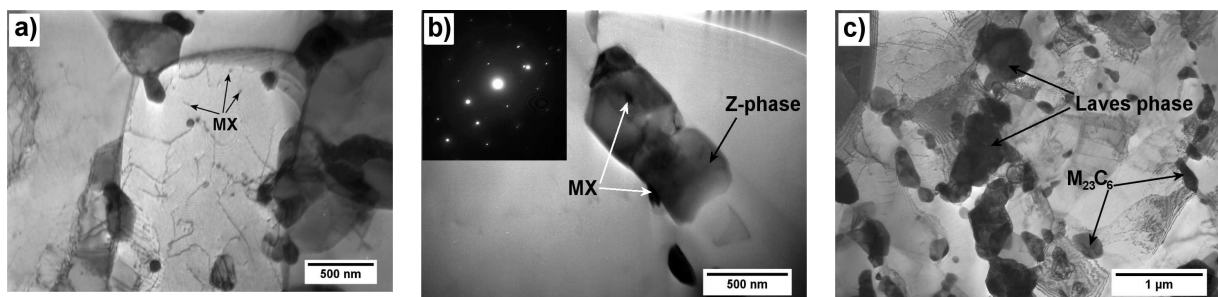
of these particles increased with prolongation of test duration. Beside Z-phase, prolongation of creep test resulted also in precipitation of much larger particles of intermetallic Laves phase, influencing a matrix solution hardening. Fig. 2c shows coarse (up to 1  $\mu\text{m}$  in diameter) Laves phase particle precipitated in the specimen deformed for 17 500h. The precipitation of the Laves phase removed Mo and W from the matrix solid solution and the strengthening of the matrix decreased.

The formation of the large particles of the Z-phase during creep exposure causes a faster creep strength degradation because its formation consumes MX precipitates. Coarsening of secondary precipitates, dissolution of MX and precipitation of large Laves- and Z phase particles decrease precipitation hardening and influence increased recovery of the VM12 steel matrix.

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**Figure 1.** TEM micrographs of the VM12 steel a) as received, b and c) crept at 625°C for 28 983h.



**Figure 2.** Microstructure showing a) fine MX within sub-grains, b) precipitates of Z-phase and MX, c) precipitates of Laves phase and  $\text{M}_{23}\text{C}_6$  carbides.