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Fine $(Cr,Fe)_2B$ borides on grain boundaries in a 10Cr–0.01B martensitic steel

I. Fedorova [a,*], F. Liu [b], F.B. Grumsen [a], Y. Cao [b], O.V. Mishin [a], J. Hald [a]

[a] Department of Mechanical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
[b] Department of Industrial and Materials Science, Chalmers University of Technology, 41296, Gothenburg, Sweden

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ABSTRACT

A 10Cr creep resistant martensitic steel with 108 ppm B was normalized at 1100 °C for 1 h and air cooled. Fine $(Cr,Fe)_2B$ borides were observed on the majority of prior austenite grain boundaries, all of which were high angle boundaries, as revealed by EBSD-based reconstruction of parent austenite grains. Some high angle boundaries including twin boundaries were boride-free. Segregation of boron to austenite grain boundaries during slow cooling from 1100 °C led to boride nucleation and growth. Their size increased with decreasing cooling rate. Borides were verified by atom probe tomography, auger spectroscopy, transmission and scanning electron microscopy.

9–12%Cr martensitic creep resistant steels are applied in pressurized steam power plant components, such as pipes, turbine casings and rotors, operating at elevated temperatures up to 620 °C. High stability of the tempered martensite microstructure under service loads is achieved by precipitation of $M_{23}C_6$ carbides, MX nitrides and intermetallic Laves phase. The presence of fine precipitates is facilitated by normalizing and tempering quality heat treatment. Normalizing consists of heating between 1020 °C and 1150 °C, whereby austenite is formed and precipitate phases are largely dissolved. During subsequent cooling, martensite transformation begins at 400 to 200 °C (mainly depending on the carbon content) and is almost complete at room temperature. The hard and brittle martensite is then softened during tempering at 620–780 °C when $M_{23}C_6$ carbides and MX nitrides precipitate [1, 2]. The addition of a small amount (about 20–150 ppm) of B has been found to significantly improve creep strength of the martensitic 9–12% Cr steels [3]. The influence of boron on creep strength is attributed to the incorporation of boron into $M_{23}(C,B)_6$ carbides during tempering, whereby their coarsening rate during creep is reduced [4–7]. However, details of boron behaviour in martensitic creep resistant steels are not well-understood.

For austenitic steels, it is well documented that boron segregates to austenite grain boundaries (GBs) during cooling after solution treatment, and that segregated boron atoms can lead to the formation of boron-rich precipitates on austenite GBs [8–12]. Similar boron segregation has also been found in 9–12%Cr steels and other martensitic steels [6, 13–15], which is to be expected, since martensitic steels are austenitic during cooling from the normalizing temperature until the martensite transformation begins. Studies of boron in 9–12%Cr steels have mainly focused on the as-tempered or creep exposed conditions [4, 16–19]. In such martensitic steels, borides have been found as large particles presumably formed from the melt during solidification, and particularly the formation of BN particles has been described in detail [4, 16, 18–21]. In the present work, we focus on studying boron behaviour at GBs in a 10%Cr steel during the normalization using a variety of advanced experimental techniques for specimen preparation and characterization.

The investigated material was taken from a large forging of a martensitic steel (9.32%Cr, 1.49%Mo, 0.05%Nb, 0.33%Mn, 0.14%C, 0.002%N, 1.25%Co, 0.2%V, and 0.0108%B, wt.% bal. Fe) after normalization and tempering quality heat treatment. A cubic sample with a side length of 15 mm was heated to 1100 °C for 1 h followed by air cooling to provoke boron segregation. Atom probe tomography (APT) was chosen for quantification of boron content at prior austenite grain boundaries (PAGBs) in a specimen prepared using in-situ lift-out method in a focused ion beam and scanning electron microscope (FIB/SEM) FEI Helios NanoLab 600. The final radius of this specimen tip was less than 50 nm. The PAGB in the APT specimen was identified by ion tunneling contrast of FIB microscopy. The PAGB was oriented 90° to the tip axis to simplify its recognition at the final tip sharpening process and also to ensure the presence of this PAGB in the final tip. Transmission Kikuchi diffraction with a step size of 10 nm was used to track the PAGB during final milling, and its misorientation angle was measured to be $\theta = 52°$. The APT analysis was performed using a local electrode atom probe Imago LEAP 3000X HR in the laser mode at −218°C with laser energy of 0.3 nJ and a pulse frequency of 200 kHz. The acquired data were

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[*] Corresponding author.
E-mail address: irfe@mek.dtu.dk (I. Fedorova).

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analyzed using IVAS 3.4.1 software from CAMECA. The reconstructed APT tip contained approximately 26 × 10^6 atoms.

The APT results reveal a conglomeration enriched by B, Cr, Fe, Mo, V, Nb and C in the vicinity of the PAGB. The distribution of B atoms is presented in Fig. 1a. The conglomeration has a semi-ellipsoid shape with a flat surface along the PAGB and a maximum thickness of 14 nm in the APT analyzed volume. The conglomeration was isolated by an isoconcentration surface (at a B concentration of 29 at.%) containing 226 × 10^3 atoms with composition: 33%B, 36%Cr, 21%Fe, 6%Mo, 2%V, 0.07%Nb and 2%C (all in at.%) (Table 1). The quantification was performed according to [22]. This composition corresponds to a M_2B-type precipitate, where M is mainly Cr, Fe and Mo atoms. 1D concentration profiles were calculated along a cylinder volume with a diameter of 10 nm perpendicular to the flat surface corresponding to the PAGB (Fig. 1b).

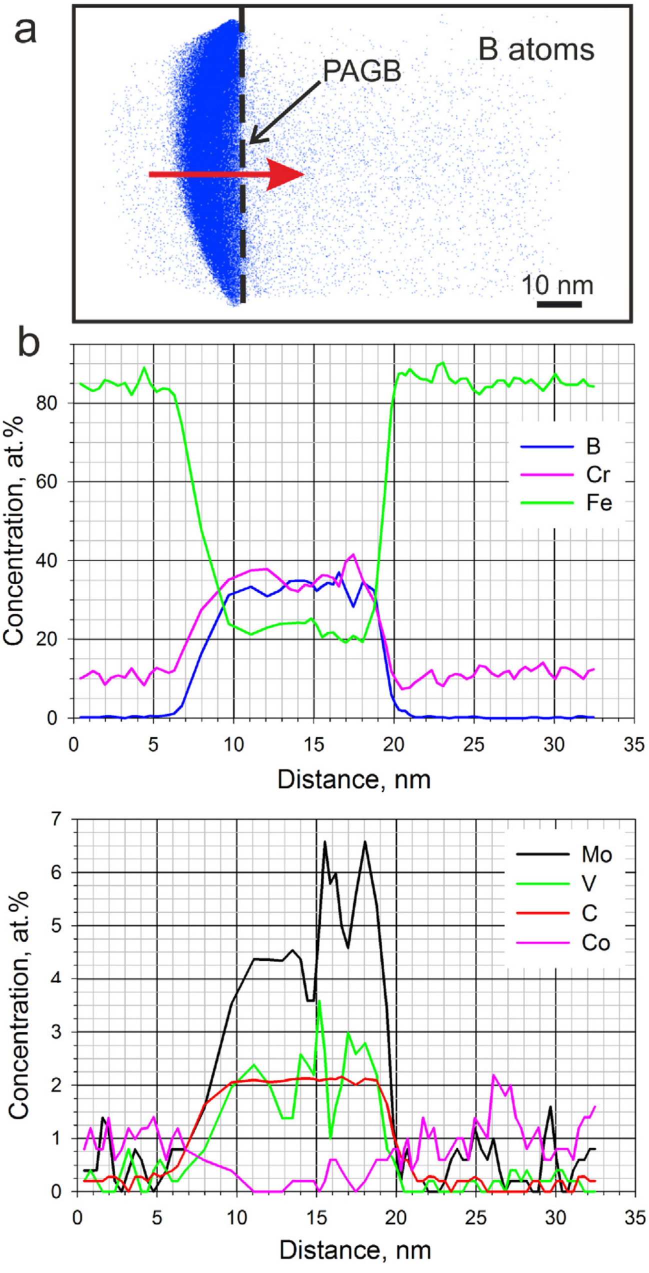

Fig. 1. APT analysis of a boride in the vicinity of a PAGB with a misorientation angle of 52°: (a) distribution of boron atoms; (b) a linear concentration profile through the boride (all in at.%).

Table 1
The chemical composition of borides analyzed by APT in present work in the 10Cr-0.01B martensitic steel and in austenitic steels studied in [23] (all in at.%).

Borides		B	Cr	Fe	Mo	C	V	Co	Nb	Mn
$M_{1.8}(B,C)$	Present work	33.0	36.1	20.9	5.2	2.1	2.3	0.2	0.07	0.2
$M_{1.7}(B,C)$	Ref. [23]	35.0	29.5	12.9	20.5	1.5	–	–	–	0.6
$M_{2.7}(B,C)$	Ref. [23]	25.2	36.0	9.8	26.8	2.2	–	–	–	–

Taking into account that fine Cr-rich borides of this type have not been previously observed in as-normalized martensitic 9–12%Cr steels, our APT results indicating the presence of the M_2B-type precipitate are surprising. In contrast to the martensitic steels, Cr-rich M_2X borides were found by atom probe in two 17Cr–13Ni austenitic steels containing 23 and 40 ppm of B [23] (see Table 1). The borides observed in both the austenitic steels and our martensitic steel contained significant amounts of carbon. Additionally, the boride in the present work is enriched by V and Nb.

To verify our findings on a larger scale, scanning electron microscopy (SEM), Auger spectroscopy on thin foil and transmission electron microscopy (TEM) on extraction replicas were applied. All techniques revealed chains of fine precipitates at PAGBs with sizes similar to the one found by APT. For Auger spectroscopy, a thin foil was prepared by jet-electropolishing in 10% perchloric acid in ethanol at −33°C and 22V using Struers “Tenupol-5”, and the measurements were made in a PHI 700 Scanning Auger electron spectroscope. A gentle argon ion sputtering was used to remove the surface contamination prior to data acquisition. The accelerating voltage was 10 kV and the beam current was 10 nA. Typical Auger spectra taken from a PAGB precipitate and matrix are presented in Fig. 2, where boron is identified in the precipitate (encircled in Fig. 2a).

More GB precipitates were investigated by energy dispersive x-ray spectroscopy (EDS) on carbon extraction replicas made by a Q150R E carbon coater and detached from the bulk by electrolytic etching in a solution of 5% hydrochloric acid in ethanol. The replicas were investigated using a JEOL 3000F field emission gun (FEG) TEM, where PAGBs were identified by the traces of triple junctions (Fig. 3a). Fine precipitates were observed only on the PAGBs, but not on martensite block, packet or lath boundaries or anywhere else within the martensite matrix. The EDS system used in the present work did not allow quantitative analysis of boron. Therefore, the average chemical composition was corrected assuming the presence of 33.3 at.% boron. The corrected average chemical composition for at least 8 randomly chosen PAGB precipitates is consistent with the APT results (Fig. 3, Table 2). The mean size of the observed borides is approximately 15 nm in width and 95 nm in length along the PAGB, i.e. they have similar thickness to that of the conglomeration observed in APT, and their length is 6 times their thickness, which is similar to borides observed by Karlsson and Nordén [23] and Sourmail et al. [24].

According to [23], the presence and the size of borides in austenitic steels were highly dependent on the cooling rate after solution treatment. In the steels investigated in [23], borides were not observed after water quenching, but were found after air and furnace cooling, and their average size increased from 50 to 700 nm with decreasing cooling rate. To investigate whether there is a similar tendency in the present martensitic creep resistant steel, normalization at 1100 °C for 1 h was followed by fast cooling in water (within 5 s) or slow cooling in furnace (within 8 h) to room temperature.

SEM observations showed behaviour similar to that in the austenitic steels: no PAGBs with borides were found in the specimen heat treated with fast cooling rate. This indicates that the borides are dissolved at 1100 °C; and that they nucleate and grow during cooling from the normalization temperature. Furthermore, it was found that slow cooling led to increased growth of PAGB borides as compared to air cooling. The mean size of the borides grown during slow cooling in furnace could not be measured on the carbon replicas because the replicas did