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Fine (Cr,Fe)₂B borides on grain boundaries in a 10Cr-0.01B martensitic steel

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Abstract

A 10Cr creep resistant martensitic steel with 108 ppm B was normalized at 1100°C for 1h 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.

Keywords: martensitic steels; borides; atom probe tomography; boron behavior

9-12%Cr martensitic creep resistant steels are applied in pressurised 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 M₂₃C₆ 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 M₂₃C₆ 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 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 $\theta = 52^\circ$. 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 analysed 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.

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

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).

Taking into account that fine Cr-rich borides of this type have not been previously observed in as-normalised 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.

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	-	-	-	-

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 -33C 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.

Fig. 2. Auger spectroscopy data from the martensitic steel containing 108 ppm of B in the as-normalized condition: (a) a region containing a PAGB, where boron-rich precipitates are seen as bright features; (b) spectra taken from the encircled areas representing a PAGB precipitate (red circle) and the martensitic matrix (black circle).

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).

Fig. 3. TEM micrographs from a carbon replica in the 10Cr-0.01B martensitic steel: (a) triple junction of PAGB traces; (b) a high magnification image showing M₂B borides in the area framed in (a) along with their chemical compositions (without B) as measured by EDS (all in at.%).

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 PGB, i.e. they have similar thickness as 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 behavior 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 they did not extract large precipitates with the technique used. Based on SEM observations, their maximum length was established to be approximately 300 nm. Thus, the evolution of borides in the austenitic steels [23] and in the present martensitic steel is qualitatively similar. The chemical composition of the borides was found to change significantly with cooling rate (see Table 2).

It is known that M_2B type borides can have tetragonal (space group 14/mcm) or orthorhombic (space group Fddd) crystal structures [12, 23, 25]. For example, Karlsson and Nordén [23] found a Mo-free M_2B phase with the orthorhombic structure and Mo containing M_2B with the tetragonal structure. Although attempts were made to identify the crystal structure of the PAGB borides by electron diffraction in our work, the diffraction patterns obtained did not match any of the suggested crystal structures. This could be due to a mixture of orthorhombic and tetragonal structures as observed in [23]. Further investigations are required to analyze the crystallography of M_2B borides and the orientation relationships between M_2B precipitates and the martensite matrix.

Table 2. Chemical composition of M_2B borides formed in the 10Cr-0.01B martensitic steel cooled either in water, air or furnace and measured by EDS on extraction replicas or by APT. The measurement results are compared with calculations by Thermocalc (all in at. %).

Measured compositions of M ₂ B							
Cooling media	Fe	Cr	B	Mo	Mn	V	Nb
water	No borides found						
air (EDS)*	30.6 ± 1.8	56.2 ± 2.1	-	9.6 ± 0.9	0	2.6 ± 0.3	1.0 ± 0.1
furnace (EDS)*	23.2 ± 1.2	58.2 ± 2.5	-	7.6 ± 0.6	0	7.4 ± 0.4	3.6 ± 0.3
air (APT)	20.9	36.1	33	5.2	0.2	2.3	0.07
air (EDS) including boron	20.4	37.5	33.3	6.4	0	1.7	0.7
furnace (EDS) including boron	15.5	38.8	33.3	5.1	0	4.9	2.4
Calculated composition of orthorhombic M ₂ B, Thermocalc TCFE9							
Temperature	Fe	Cr	B	Mo	Mn	V	Nb
1100°C	31.2	32.4	33.3	2.6	0.33	-	-
700°C	20.5	35.4	33.3	10.5	0.29	-	-
606°C	15.5	32.6	33.3	18.4	0.24	-	-

*- average values calculated based on 8 randomly chosen precipitates.

Phase equilibrium calculations made for the present steel composition using Thermo-Calc version 2017b with the TCFE9 database [26] predict that orthorhombic M₂B is stable in the temperature range from 1200°C to 1160°C. Below 1160°C a molybdenum-rich M₃B₂ with D5A crystal structure is predicted to be the most stable boride. However, when M₃B₂ is suspended from the equilibrium calculations, thus simulating a situation where M₃B₂ cannot nucleate, orthorhombic M₂B is predicted to be stable. When the orthorhombic M₂B is then suspended, the tetragonal M₂B structure becomes stable. Comparing measured and calculated compositions, the calculated M₃B₂ and tetragonal M₂B compositions are found to contain far too much Mo. The existing thermodynamic model for orthorhombic M₂B gives a better agreement, though it has no description for V, Nb and C contents in the phase (Table 2).

As seen in Table 2, there is a good agreement between boride compositions measured by APT and EDS in the sample after air cooling and the calculated equilibrium composition at 700°C. The boride composition measured by EDS in the sample after furnace cooling shows a reasonable agreement with the equilibrium composition calculated slightly above 600°C (with austenite

selected as the matrix phase). This suggests that nucleation and growth of the borides during furnace cooling occurred at lower temperatures than during air cooling.

Furthermore, the equilibrium calculations show that for the present steel composition the solubility of boron in austenite is only 17 ppm at 1100°C. Since the heat treatment with water cooling showed that the fine GB borides were dissolved at 1100°C, it is proposed that the local concentration of boron at the austenite grain boundaries was much smaller than the total 108 ppm of boron in the steel. This indicates that a large part of the boron in the steel is tied up in large primary boron enriched particles formed during solidification or forging [16, 20].

In the present steel, SEM investigations revealed borides on most of the PAGBs both for air cooling and furnace cooling, where the average size of austenite grains was approximately 100 µm. The number of boundaries with borides in our work is much higher than in a 25Cr-22Ni austenitic steel containing 27 ppm B after solution treatment 1160°C and cooling at ~10°C/s to 1060°C followed by water quenching [24], where Cr₂B particles were observed only on a few austenite GBs. In [23] the density of fine boride precipitates was found to be similar at all grain boundaries for the 40 ppm B austenitic steel cooled at 13°C/s from 1250°C and for the 23 ppm boron steel cooled at 31°C/s from 1250°C.

To investigate any sensitivity of boride precipitation to the GB misorientation in the present martensitic steel, electron backscatter diffraction (EBSD) with a step size of 150 nm was performed in a Zeiss 35 Supra FEGSEM. The investigated region contained several prior austenite grains (PAGs), with martensite blocks, packets and laths (Fig. 4a). In this region, precipitates were found on a number of PAGBs (exemplified in Fig. 4b). Parent austenite grains were then reconstructed from the EBSD data using the ARPGE software [27] and applying Nishiyama–Wasserman orientation relationships. The result of this reconstruction is presented in Fig. 4(c), where it is seen that reconstructed austenite GBs are boundaries with misorientation angles between 21° and 60°. Analysis of the reconstructed austenite GBs did not reveal correlations between their misorientations and the presence of fine borides, except for twin boundaries which were all boride-free.

The absence of borides on some PAGBs can be attributed to suppressed nucleation, where GB plane orientation is the main controlling factor as suggested in [23]. As follows from the observation of the flat interface in Fig. 1a, the borides need GB planes, where they can form coherent or semi-coherent interfaces, in order to ease nucleation.

Fig. 4. One region investigated using both BSE and EBSD: (a) EBSD map, where high angle boundaries are shown as black lines; (b) a high magnification BSE image of the area framed in (a), which contains one boride-free PAGB and two PAGBs with borides seen as bright features; (c) Parent austenite grains reconstructed using the ARPGE software. Boundaries identified as $\Sigma 3$ twin boundaries are shown as red lines. Deviations from the straight twin boundary morphology are reconstruction artifacts. Angles of misorientations between the reconstructed austenite grains 1 to 8 are shown on the right-hand side.

The observed formation of fine $(\text{Cr,Fe})_2\text{B}$ borides on GBs during normalization will influence the subsequent nucleation and growth of $\text{M}_{23}(\text{C,B})_6$ carbides on PAGBs during tempering and creep. The borides could enhance nucleation of carbides by acting as nucleation sites, and they can delay the carbide growth, both by blocking grain boundary diffusion and by hard impingement with the carbides. Abe [28] observed retarded growth of $\text{M}_{23}(\text{C,B})_6$ carbides on PAGBs during ageing for more than 10,000 hours at 650°C in 9%Cr steels with boron contents of 100 ppm and

more. The resulting retarded carbide growth can in turn significantly affect the mechanical properties of martensitic steels, in particular, their creep resistance.

In summary, advanced techniques, such as APT, FIB and Auger spectroscopy were applied to locally detect small concentrations of boron at PAGBs in a 10Cr martensitic creep resistant steel containing 108 ppm of B. A M_2B boride with composition: 33%B, 36%Cr, 21%Fe, 6 %Mo, 2%V, 0.07%Nb and 2%C (all in at. %) was found by APT at a PAGB after normalizing at 1100°C and cooling in air. Borides with similar sizes and compositions were found by Auger spectroscopy, SEM and TEM. The majority of of the PAGBs identified using SEM were decorated by fine borides with an average size of 95×15 nm. Reconstruction of parent austenite grains based on the EBSD data revealed boride-rich and boride-free high angle GBs. Twin boundaries within reconstructed austenite grains were boride-free. A strong influence of the cooling rate was found on boride formation: water cooling suppressed boride formation, while slower cooling led to enhanced growth of the borides. It is concluded that the fine PAGB M_2B borides were absent at 1100°C and that they nucleate and grow after boron segregates to austenite GBs during cooling from the normalization temperature. A reasonable agreement was obtained between measured compositions of the borides and compositions obtained by phase equilibrium calculations.

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