High-resolution characterization of the martensite-austenite constituent in a carbide-free bainitic steel

Christina Hofer[a,*], Vitaliy Bliznuk[b], An Verdiere[b], Roumen Petrov[b,c], Florian Winkelhofer[d], Helmut Clemens[a], Sophie Primig[a,e]

[a] Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria
[b] Department of Electrical Energy, Metals, Mechanical Constructions and Systems, Ghent University, Tech Lane Ghent Science Park – Campus A, Technologiepark 903, 9052 Zwijnaarde, Ghent, Belgium
[c] Department Materials Science and Engineering, TU Delft, Mekelweg 2, 2628 CD Delft, The Netherlands
[d] Research and Development – Business Unit Coil, voestalpine Stahl GmbH, voestalpine-Strasse 3, 4020 Linz, Austria
[e] School of Materials Science & Engineering, UNSW Sydney, 2052 NSW, Australia

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ABSTRACT

The multiphase microstructure of carbide-free bainitic steels comprises bainitic ferrite laths, retained austenite with different morphologies, a minor fraction of carbides and so-called martensite-austenite areas, which partially transform during the last cooling step. While the other constituent received much attention, little is known about the structure of the martensite-austenite constituent in carbide-free bainitic steels. Thus, in this study, it was structurally and chemically investigated by high-resolution techniques such as transmission electron microscopy and atom probe tomography after preceded unambiguous identification by electron backscatter diffraction in conventional as well as transmission mode. The results, ranging from carbon segregation to cementite precipitation in the martensitic part, indicate strong auto-tempering during final cooling which is followed by aging. Also, some kind of structural modulation in the austenite belonging to the martensite-austenite areas was observed. Atom probe tomography revealed a heterogeneous carbon distribution, further supporting the findings by transmission electron microscopy.

1. Introduction

Increasing demands on safety and energy efficiency in the automotive industry require new high-strength steels that still can be produced economically. In recent years, quenching-and-partitioning (Q&P) as well as carbide-free bainitic steels have shown to meet these requirements owing to their complex microstructure and resulting mechanical properties, e.g. see [1–4]. The combination of a hard matrix and a soft second phase accomplishes high strength with good elongation at the same time. Unlike dual-phase steels, where the hard and soft phase are both present in polygonal form, Q&P and carbide-free bainitic steels exhibit very homogeneous and fine acicular microstructures. This additionally enhances the impact toughness, impedes crack initiation and improves formability [5].

Beside their economic alloying concept, carbide-free bainitic steels also have a straightforward heat treatment. They are produced via austenitization followed by an isothermal heat treatment in the bainitic temperature range between 300 and 450 °C. During the isothermal holding time, austenite transforms into carbon-supersaturated bainite. Since bainitic ferrite can only accommodate very low amounts of carbon interstitially, the excess carbon diffuses out of the bainitic ferrite sub-units directly after their formation. Due to the high silicon content (1.5–2 m.%), which has very low solubility in cementite, the driving force for cementite precipitation is drastically reduced, leading to an effective suppression of its formation during short holding times and moderate carbon supersaturation [6]. Therefore, the carbon is available to enrich the remaining austenite [1,2,6–10]. The nm-sized austenite films between individual bainitic ferrite sub-units become highly enriched in carbon, whereas carbon partitioning into blocky austenite areas in between single sheaves of bainite progresses to a far lesser extent. Thus, in these areas lower carbon contents persist [11]. Upon further cooling, the highly enriched films of austenite remain stable until room temperature, but parts of the blocky austenite may transform to martensite, forming the so-called martensite-austenite (M-A) constituent.

Although the M-A constituent represents a small fraction of the

microstructure, it has a significant impact on the mechanical properties of the final steel product. It has been shown that large areas of M-A constituent dramatically decrease the impact toughness of the steel because they act as crack initiation sites [12–14]. The reasons therefore either lie in the high brittleness of the freshly formed plate-type martensite or in the stresses induced by the volume increase due to the martensitic transformation [12]. However, Lan et al. [15] found that very small areas of M-A constituent ($< 1\,\mu m$) can effectively inhibit crack propagation by deflection of the crack and, therefore, increase the impact toughness. Nevertheless, it should be kept in mind that further factors such as carbides and bainite packet size influence the toughness.

As a result of the carbon redistribution during the bainitic transformation, M-A areas have an elevated carbon content compared to their nominal composition which was verified by electron probe microanalysis [16–18] and atom probe tomography (APT) [19]. The boundaries remain partly austenitic whereby the center is mainly martensitic according to electron backscatter diffraction (EBSD), where the M-A areas are identified based on their lower diffraction pattern quality which results from the higher dislocation density [18–20].

Transmission electron microscopy (TEM) investigations revealed that the martensitic center of the M-A areas consists of plate martensite made up of micro-twins [12,13,15–17]. However, the identification of the M-A constituent in the TEM is not straightforward, since phase identification solely based on the contrast in bright field mode is not possible, considering that contrast changes according to the crystal orientation upon tilting. This issue can be overcome by the identification of the M-A constituent in the scanning electron microscope (SEM) by means of an EBSD scan. Subsequently, a site-specific specimen preparation can be carried out in the focused ion beam (FIB) microscope, applying the lift-out technique [21]. However, this has the disadvantage that the bombardment and implantation of the area of interest with focused ions can lead to the transformation of meta-stable retained austenite even at low voltage and current [22,23], and therefore distorts the observed results.

Since there is still a lack of information regarding the structure and composition of the M-A constituent in low carbon steels, this study aims to provide new information by high-resolution microscopy of this complex feature in a carbide-free bainitic steel. Based on the correlative microscopy approach suggested by the authors in previous work [24], where the M-A areas were unambiguously identified on a conventional TEM specimen by transmission Kikuchi diffraction (TKD) [25–27] in the SEM prior to TEM investigations, a detailed TEM diffraction study of the M-A areas is presented in this paper. Thereby, the M-A constituent was also identified based on their lower diffraction pattern quality (as in conventional EBSD), and subsequently the very same area was investigated by TEM. By application of this correlative approach, new insights into the structure of these complex features have been gained. Additionally, an attempt was made to prove the findings of the TEM investigations by APT, which is the only method for chemical analysis at the atomic scale.

2. Experimental

The chemical composition (in at.% and m.%) of the studied carbide-free bainitic steel is given in Table 1. The material was provided as industrial grade in the form of cold-rolled sheets with a thickness of 1.2 mm. The inductive heat treatment of samples with a size of

Table 1
Chemical composition of the investigated Fe-0.2C-1.5Si-2.5Mn steel in m.% and at.%.

	Fe	Mn	Si	C
M.%	Bal.	2.47	1.51	0.22
At.%	Bal.	2.45	2.93	1.00

$10 \times 5 \times 1.2\,mm^3$ was carried out in a dilatometer DIL805A from TA Instruments using a type S thermocouple. Full austenitization at 900 °C for 60 s was followed by quenching to an isothermal holding temperature of 400 °C, which is about 50 °C above the martensite start (M_s) temperature [19]. The samples were held in the bainitic temperature range for 1000 s, and subsequently quenched to room temperature. Quenching was carried out with helium gas and a cooling rate of 100 °C/s to prevent other phase transformations.

The microstructure was examined by light optical microscopy (LOM) after LePera etching [28] following the practical procedure described in [19].

TEM specimens of the as-heat treated material were prepared by mechanically thinning the sheets to a thickness of 100 μm. Then, disks with a diameter of 3 mm were punched out and electropolished with a TenuPol-5 twin-jet polisher from Struers. A solution of 4 vol% perchloric acid and 96 vol% acetic acid (CH_3COOH) and a voltage of 15 V with a flow rate of 10 at room temperature were found to be best suitable. Prior to the TEM investigations the specimens were investigated via TKD in a SEM to identify the M-A constituent with the detailed set-up reported elsewhere [24]. For EBSD and TKD analyses either a field-emission gun SEM Quanta 450 or a dual-beam SEM/FIB Versa 3D from FEI equipped with a Hikari XP EBSD system from EDAX were used. TKD scans were carried out at an effective tilt angle of $-10°$ to the incident electron beam at a working distance of 6 mm with an acceleration voltage of 30 kV, a spot size of 5, a step size of 60 nm, and 4×4 binning. Subsequently, the same regions on the sample were investigated in a JEM-2200FS TEM from JEOL equipped with a C_s corrector for the objective lens operated at a voltage of 200 kV. The schematic spot diffraction patterns were simulated with the software JEMS and the stereographic projection with the software ELDIST [29]. Cementite was described by the space group *Pbnm* with the lattice parameters a = 4.5230 Å, b = 5.0890 Å and c = 6.7428 Å.

For APT investigations the M-A constituent was identified by means of conventional EBSD on a bulk sample prior to the site-specific tip preparation in the SEM/FIB. After grinding and polishing, the samples were electropolished with a Lectro-Pol V from Struers for 10 s using the A2 electrolyte, a voltage of 40 V and a flow rate of 10. The resulting surface relief was removed by gently polishing the surface with OP-U for 20 min according to [30]. The EBSD measurements were performed at a working distance of 15 mm with an acceleration voltage of 20 kV, 2 nA current and 6×6 binning. First an overview scan was carried out to identify areas of interest and then a detailed scan with a size of $9 \times 9\,\mu m^2$ and a smaller step size of 25 nm was conducted. The data evaluation for both EBSD and TKD was carried out with the TSL OIM Analysis 7 software without using any data clean-ups. The chemical composition of the M-A constituent was determined by APT investigations after extraction of the area of interest in the FIB by means of the standard lift-out method [31]. The last step of the annular milling was performed at 5 kV to minimize gallium implantation. APT was carried out using a local electrode atom probe (Cameca, LEAP 3000X HR) in the voltage mode with a pulse repetition rate of 200 kHz, a pulse fraction of 0.2 and a specimen temperature of 60 K. Imago Visualization and Analysis Software (IVAS) version 3.6 was used for all analyses.

3. Results and Discussion

The holding time for isothermal bainitic transformation at 400 °C in the dilatometer was selected sufficiently long (1000 s) in order to complete the bainitic transformation. Thus, no reaction during the second quenching step from this temperature to room temperature was observed, indicating a fully bainitic microstructure. This was also proven by LOM and SEM images, as shown in Fig. 1. The microstructure after etching with LePera is shown in Fig. 1a, where the dark areas correspond to carbide-free bainite and the white and light brown areas reveal the retained austenite and the M-A constituent, which cannot be distinguished using this etchant. In Fig. 1b a SEM image of the same