

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: <http://www.elsevier.com/locate/acme>

Original Research Article

Development of the low temperature bainite

Mohamed Soliman^{*}, Heinz Palkowski

Institute of Metallurgy, Clausthal University of Technology, Robert-Koch-Strasse, 42, 38678 Clausthal-Zellerfeld, Germany

ARTICLE INFO

Article history:

Received 5 October 2015

Accepted 20 February 2016

Available online 9 March 2016

Keywords:

Low temperature bainite

Alloy design

Thermo-mechanical processing

Bake hardening

ABSTRACT

The possibility of obtaining steels with nano-size plates of bainitic-ferrite by isothermal transformation at low temperature is set forth. These steels have attracted great interest due to their excellent combination of strength, toughness, and ductility. In further investigations, the composition and the processing methods of these steels are adjusted to: (1) Optimize their technological properties with regard to mechanical behavior, weldability and formability. (2) Accelerate their transformation kinetics. (3) Minimize/eliminate the need for expensive alloying elements. (4) Lower the martensite start temperature (M_s) either by thermo-mechanical processing or by modifying the bainite transformation stage. Suppressing M_s is of particular importance in steels with relatively low carbon content; that is to allow for bainite formation at low temperature. Furthermore, many reports addressed some technological aspects like fatigue behavior, wear resistance and bake hardenability. This article presents an overview of the so far studied alloying strategies and processing methods adopted for developing the low temperature bainite together with addressing some examined technological themes. The paper is engrafted in relevant sections with new results of the authors that are not published before. One of these results is that the low temperature bainite possesses a very strong bake hardening potential.

© 2016 Politechnika Wroclawska. Published by Elsevier Sp. z o.o. All rights reserved.

1. From carbide-free bainite to low temperature bainite

Since the discovery of carbide-free bainite microstructures with both high strength and high toughness in the 1980s [1,2], carbide-free bainitic steels have been widely manufactured and applied in many industrial fields, such as car, gear, railway, and many others [3–6]. The production of carbide-free bainite microstructure is realized by the suppression of cementite precipitation during the bainite transformation

through adequate addition of elements like silicon and aluminum. These elements have very low solubility in cementite. Simultaneously, the mobility of these substitutional atoms at the temperature of bainite formation is limited. The atoms of cementite suppressing elements must then become trapped in the untransformed austenite during the para-equilibrium formation of bainitic ferrite. Ultimately, the cementite formation is suppressed.

The absence of cementite ensures that the carbon enriches the austenite rather than forming cementite plates. This results in lowering the martensite start temperature (M_s).

^{*} Corresponding author. Tel.: +49 5323723876; fax: +49 5323 3527.

E-mail addresses: mohamed.soliman@tu-clausthal.de (M. Soliman), heinz.palkowski@tu-clausthal.de (H. Palkowski).

<http://dx.doi.org/10.1016/j.acme.2016.02.007>

1644-9665/© 2016 Politechnika Wroclawska. Published by Elsevier Sp. z o.o. All rights reserved.

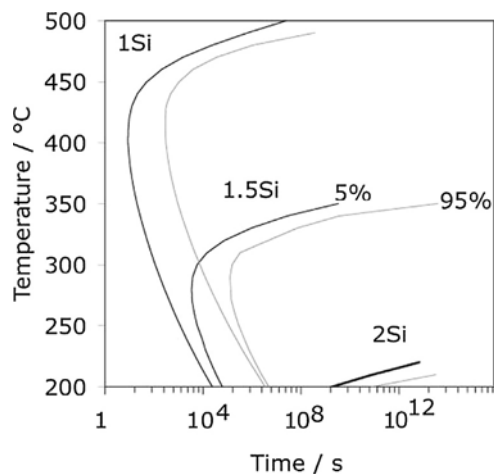


Fig. 1 – Predicted time–temperature–precipitation diagram for para-equilibrium cementite in system Fe–Si–Mn–C with base composition Fe–1.2C–1.5Mn–1.5Si (percentages represent the portion of cementite precipitations being completed) [7].

Therefore, after the course of bainite transformation, a certain amount of austenite can be stabilized to room temperature (RT); this austenite is known as retained austenite. Thus, the final microstructure consists of bainitic ferrite and high carbon retained austenite. However, the calculations of Kozeschnik and Bhadeshia demonstrated that silicon is ineffective in retarding the precipitation of cementite if the parent phase is highly supersaturated with carbon. This is because the driving force for the reaction is large even for para-equilibrium precipitation [7]. Fig. 1 illustrates the predicted time–temperature–precipitation (TTP) diagram for the precipitation of cementite from austenite saturated with 1.2 wt% C at different Si contents.

Reliant on the conception of carbide-free bainite, in combination with allowing for high carbon content and performing the bainitic transformation at low temperature, Sandvik and Nevalainen [1] were the first to obtain ultra-fine bainite with high strength and ductility. They obtained this novel structure through isothermal transformation of austenite at low-temperature conditions in some high-carbon high-silicon steels [1]. Bhadeshia and collaborators set forth investigation on low-temperature bainite (LTB) by modifying the steel composition, addressing the fundamental mechanisms behind its nanostructure along with studying factors determining its mechanical behavior and detailed characterization of its microstructure development [8–13]. Their study attracted great interest due to the excellent combination of strength, toughness, and ductility. The evolution of the mechanical properties evaluations of the novel bainitic steels has revealed ultimate tensile strength (UTS) of about 2.2 GPa, hardness values in the range of 600–670 HV, a noticeable uniform elongation in the range of 5–30% as well as fracture toughness up to $130 \text{ MPa m}^{1/2}$.

These steels satisfy the ever-increasing demands for advanced materials fulfilling the demands for both high strength and high toughness in application fields such as

Table 1 – Typical chemical compositions of the previous novel bainitic steels (wt%) [9,11].

| C | Si | Mn | Al | Cr | Mo | Co | Balance |
|-----|-----|-----|-----|-----|------|-----|---------|
| 0.8 | 1.6 | 2.0 | – | 1.0 | 0.25 | 1.5 | Fe |
| 0.8 | 1.5 | 2.0 | 1.0 | 1.0 | 0.25 | 1.5 | Fe |

automotive and railway industries. The material is now commercially available and the manufacturing process established to a point where hundreds of tons have been produced successfully [14].

2. The first generation of low temperature bainite

The key to the excellent properties of LTB is a fine-scale microstructure consisting of nanoscale bainitic-ferrite and thin films of retained austenite. To obtain these microstructures, it is necessary to carry out the bainitic transformation at low temperatures. Table 1 shows a first generation of LTB with each elemental addition having a specific intended role [9,11]. High carbon content is considered as a key requirement, which suppresses the M_s to allow carrying out the bainite transformation at low temperature. In addition, a high Si content is needed to suppress cementite precipitation. Cementite is a crack initiation phase that should be avoided in high strength steels. Hardenability is increased via Mn and Cr additions [8–11]. Al and Co are added to accelerate the kinetics of the bainite transformation; that is because at low reaction temperatures the rate of transformation is very slow, sometimes taking days to achieve the maximum fraction of bainitic ferrite [9]. The addition of these two elements is the difference between the early alloys studied by Bhadeshia and the earlier ones of Sandvik and Nevalainen.

3. Newly designed alloys of low temperature bainite

Subsequently, much research in the area has focused on experimentally varying the chemistry, transformation time and temperature to achieve certain levels of strength and ductility. Examples of the investigated chemistries are given in Table 2.

Yoozbashi and Yazdani [15] designed a new nanostructured bainitic steel (alloy A) by decreasing the Co and C content and modifying the contents of Mn and Cr in order to reduce the alloy costs. The authors used the electro-slag remelting (ESR) process to improve the cleanness of the steel. Yang et al. [16] added Al instead of Co (alloy B) to accelerate the bainitic transformation and avoid carbides precipitation and added W instead of Mo to prevent temper embrittlement. Temper embrittlement is caused by the presence of specific impurities in the steel, which segregate to prior austenite grain boundaries during heat treatment. The W atom is very large relative to other alloying elements and impurities. It effectively impedes the migration of those elements and thereby provides resistance to temper embrittlement.

Table 2 – Chemical compositions, transformation times and temperatures and the obtained properties: Ultimate- and yield strength (UTS and YS) (MPa), elongation to rupture TEL (%), impact toughness I (J) and Vickers hardness HV. Alloys D and F are protected by patents indicated in Refs. [18,20], respectively.

| Alloy | C | Si | Mn | Al | Cr | Mo | Co | V | W | T (°C)/t (h) | UTS/YS | I/TEL | HV |
|--------|------|------|------|------|------|------|------|-----|------|---|-------------------------------------|---------------------------|-------------------|
| A [15] | 0.69 | 1.92 | 1.38 | 0.75 | 1.39 | 0.24 | 0.14 | | | 300/8 250/20 | ~1600/- ~1850/- | -/~32 -/~23 | - |
| B [16] | 0.83 | 1.56 | 1.37 | 1.44 | 0.81 | - | - | - | 0.87 | 260/4 240/12 220/24 | 2080/1534 2139/1826 2375/1955 | 7.8/- 6.8/- 6.7/- | - |
| C [17] | 0.8 | 1.9 | 0.1 | 0.7 | 1.9 | 0.25 | - | | | 300/6 250/16 200/72 | - - - | - - - | 570 660 690 |
| D [18] | 0.79 | 1.55 | 1.00 | - | 1.01 | 0.25 | - | 0.1 | | 250/8 200/24 | 2098/1673 1981/1678 | -/8 -/4.3 | 640 690 |
| E [19] | 0.67 | 2.10 | 0.92 | 0.90 | 1.30 | 0.24 | 1.73 | - | | 300/2.5 250/5.5 | 1916/1580 2236/1720 | -/8.8 -/7.6 | 554 638 |
| F [20] | 0.55 | 2.1 | 0.37 | 0.90 | 1.47 | 0.46 | 1.8 | - | | 320/0.5 300/0.8 300-(0.02 K s ⁻¹) | 1915/1350 2062/1620 2090/1420 | -/10.5 -/10.2 -/7.5 | 559 600 610 |
| G [21] | 1.15 | 2.15 | - | 0.89 | 0.58 | 0.25 | 1.58 | - | - | 300/~5 250/~50 200/~250 | - - - | - - - | 623 653 694 |

The yield strength and the ultimate tensile strength ranged between 1534–1955 MPa and 2080–2375 MPa, respectively, with a total elongation of 6.7–7.8%. Huang et al. [17] investigated 729 possible alloys and their ability to produce carbide-free nanostructured bainite using thermodynamic calculations in combination with a neural network model. They set C = 0.7 wt % and systematically studied combinations of low, middle and high concentrations of Si, Mn, Al, Cr, Mo and Co by means of driving force calculations. Their computation of time–temperature–transformation (TTT) diagrams indicated that there is still the possibility to accelerate the transformation kinetics. An important conclusion of their study was that reducing Mn has a much greater effect than increasing Co in terms of accelerating the bainite reaction which can bring significant cost reductions. In this alloy, a higher level of Cr is used to compensate the hardenability loss due to lower Mn content as it has little effect on $\Delta G^{\gamma-\alpha}$. So far, the authors have published only the hardness property of their steel.

In an earlier work of Bhadeshia et al. [18] decreasing the Mn content to 1 wt% (alloy D) is adopted. The steel incorporates V being useful in controlling the austenite grain size during austenitization via pinning the austenite grain boundaries with the aid of VC precipitates. Refining the austenite grain size accelerates the bainite transformation kinetics. This effect is attributed to the increase in the number density of austenite grain boundary nucleation sites caused by grain refinement [9]. The authors of the patented alloy D were able to achieve ultimate tensile strengths more than 2.0 GPa in a Co free steel within a transformation time of 8 h.

In alloys E, F and G Al and Co are added to accelerate the bainite transformation and Mn is set to 0.9 wt%, 0.3 wt% and 0 wt%, respectively [19–21]. Decreasing/removal of Mn has a twofold effect:

(1) Shifting the T₀ curve to the right, which increases the degree of bainite transformation possible, i.e. increases the quantity of the produced strong bainite at a given transformation temperature. The T₀ curve is the locus of

the maximum C concentration that can saturate the retained austenite, C_γ, at a given bainite transformation temperature [22].

(2) Lowering the thermal stability of the retained austenite, which increases the transformation rate. Huang et al. revealed that Mn reduction appears to be the most effective mean to accelerate bainite formation at low temperatures [17]. In alloy G, the effect of Mn removal on the material hardenability is counteracted by increasing the carbon content [21]. Alloy G is found to achieve a hardness value of 694 HV after treatment at 200 °C for about 10 days.

In alloy F, another alternative for accelerating the bainite transformation with a decreased C content is applied. Both, bainite formation rate and its total amount, increase as a result of decreasing the C content. Of course, the reduction of the C content of the alloy is only as long useful as not leading to an unacceptable decrease in strength of the steel, i.e. by coarsening. Our team learned that in medium C steels with C between 0.5 wt% and 0.7 wt%, the bainite microstructure after heat treatment in a low temperature range have the optimized mechanical properties. A higher C concentration reduces the maximum attainable volume fraction of the strong bainitic ferrite [23]. In contrast, a lower C concentration increases the minimum transformation temperature for bainite formation caused by an increased Ms, which consequently leads to a coarser bainite microstructure and losing the high strength of the low temperature bainite. Fig. 2a shows the amount of C that can enrich the austenite during the bainite formation process, i.e. the T₀ curve, drawn for steels E and F using Thermo-Calc software using TCFE7 database. According to the T₀ concept, the maximum fraction of bainite (V_b) that can be obtained at any temperature is also limited according to the equation [22]:

$$V_b = \frac{C_\gamma - \bar{C}}{C_\gamma - s} \quad (1)$$

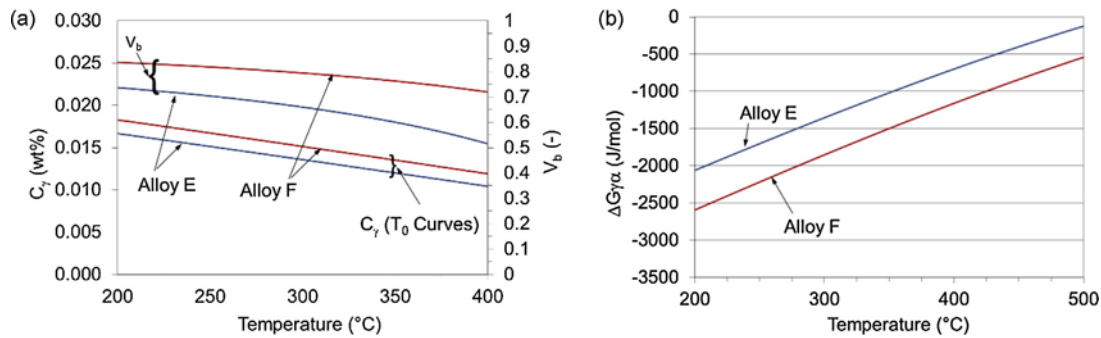


Fig. 2 – (a) Theoretical dependence of the carbon concentration in austenite and bainite volume fraction on the transformation temperature. (b) Driving force of transformation from austenite to ferrite ($\Delta G^{\gamma\alpha}$) for the two illustrative examples – original.

where, \bar{C} is the carbon concentration of the alloy and “s” is the amount of carbon trapped in the bainite-ferrite in the form of solid solution and carbides.

Eq. (1) suggests two main methods of increasing the maximum permitted volume fraction of the bainite “ V_b ”:

- (i) reducing the alloy carbon concentration and
- (ii) modifying the concentration of substitutional alloying elements such that the T_0 curve is shifted to higher austenite carbon concentration (increasing “ C_γ ”).

According to Aaronson et al. [24], manganese has the strongest effect in shifting the T_0 boundary to lower carbon concentrations; thereby decreasing its content facilitates the enrichment of the austenite with C and hence formation of a greater volume fraction of bainitic-ferrite, V_b , according to Eq. (1). Fig. 2a shows a plot of the theoretical dependence of V_b on the bainite transformation temperature of alloys E and F. Both decreasing the C and Mn contents of alloy F increased the quantity of the strong bainite ferrite.

The method of invention of alloy F includes also maximizing the driving force of the transformation from austenite to the bainitic ferrite ($\Delta G^{\gamma\alpha}$), so as to accelerate the transformation. Fig. 2b shows that alloy F achieves a higher driving force than alloy E.

The increased Mo in alloy F is to compensate for the hardenability decrease due to the reduced Mn and C content. Dissolved Mo dramatically retards the transformation of austenite into ferrite and pearlite. It has, however, no big influence on the transformation rate of austenite to bainite [25]. In a particular case a tensile strength above 2 GPa is produced in LTB within a transformation time of 50 min. The properties are achieved in commercial purity steel melted in air. The fast transformation permits the production of LTB in

short transformation cycles associating with continuous cooling processes in stacks of large thick products or in a coiled strip.

4. LTB in low to medium carbon steels

One critical issue with the steels containing higher C content is their poor weldability. Low carbon steels are therefore preferable for structural components that require welding. Accordingly, many efforts have been devoted to design LTB with low-to-medium C bainitic steels. The new compositions contain up to 0.4 wt% C. This modification was successful because of the fact that much of the strength of the fine bainite comes from its fine scale and not from dissolved C [22,23].

The first attempt in this field was by Yang and Bhadeshia [26]. They reduced the C concentration and used Ni as a substitutional solute to suppress the M_s . They studied three alloys containing 4 wt%, 5 wt% and 6.7 wt% Ni. It was possible to perform the bainite transformation at low temperatures only in the alloy with 6.7% Ni (alloy H in Table 3). The other alloys have a M_s above 370 °C. Dilatometric data from isothermal transformation experiments of this alloy showed a small amount of transformation even after a prolonged holding period of 31 h at 280 °C to establish that bainite can form. They concluded that the M_s can indeed be suppressed by increasing the Ni content but unlike the high carbon steels, the difference between the bainite start temperature (B_s) and M_s decreases dramatically. At high solute concentrations, this difference approaches zero which means the formation of bainite is not possible.

The first successfully produced LTB in low carbon steel was done by Soliman et al. [27]. In alloy I (Table 3) Ni was added and

Table 3 – Studied compositions (wt%) for obtaining LTB in low to medium carbon steels. The balance is Fe.

| Alloy | C | Si | Mn | Al | Cr | Mo | Co | Ni |
|-----------|------|------|------|------|------|------|------|------|
| H [26] | 0.20 | 1.5 | 2.5 | – | – | – | – | 6.7 |
| I [27] | 0.26 | 1.65 | 3.44 | 0.9 | 1.14 | 0.25 | 0.49 | 1.85 |
| J [28] | 0.28 | 0.67 | 1.96 | 1.19 | 1.62 | 0.23 | – | 0.34 |
| K [29,30] | 0.35 | 1.48 | 1.52 | 0.76 | 1.15 | 0.4 | – | 0.93 |
| L [31] | 0.40 | 1.8 | 2.8 | – | – | – | – | – |

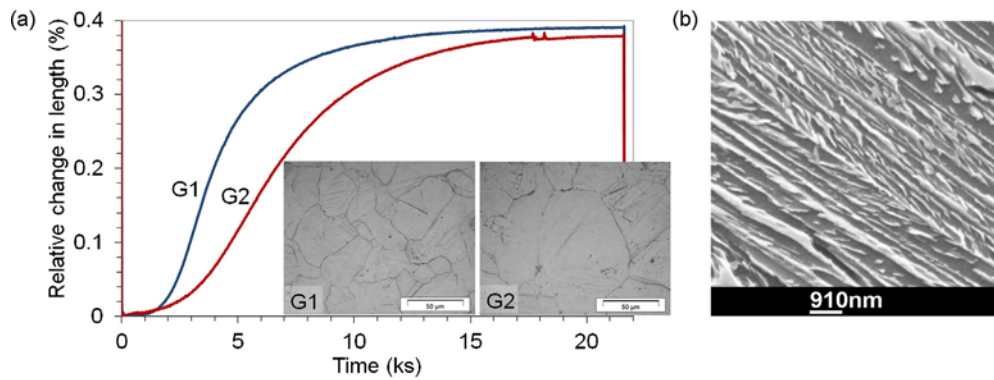


Fig. 3 – Kinetics of bainite transformation at 305 °C of alloy I (Table 3) with two prior austenite grain sizes G1 and G2 together with a scanning electron micrograph of obtained structure from G2 – original.

the Mn level was increased to suppress the Ms. Al and Co was added to accelerate the bainite transformation kinetics. The steel was austenitized at 950 °C for 30 min. The measured Ms of this alloy was 284 °C, consequently LTB could be produced at a temperature of 305 °C. Fig. 3a presents the real time monitoring of the bainite transformation kinetics presented in terms of relative change in length for alloy I with two different prior austenite grain size (PAGS) of G1 = 25 and G2 = 50 μm. The time required for the cessation of bainite transformation at this temperature recorded, in both cases, about 6 h. It is clear from Fig. 3a that the transformation in smaller grained material started faster, but proceeds, before the end of the transformation, at a slower rate. Indeed, the grain-size reduction causes an increase in the total grain-boundary area, at which the first bainitic ferrite subunits nucleate. Thus, the transformation starts more quickly, due to an enhanced nucleation rate. The transformation then proceeds by means of nucleation and growth of new subunits from the tip of the previous ones toward the interior of the austenite grain; thus, when the austenite grain size is reduced, the transformation proceeds at a slower rate.

Fig. 3b shows a scanning electron micrograph of the obtained structure from G2. Ultimate and yield strengths in compression of this alloy recorded about 2058 MPa and 1300 MPa, respectively. A wide spectrum of mechanical properties and getting generation of LTB below Ms of the bulk material are obtained by applying various heat treatment techniques as will be shown later.

Qian et al. [28] demonstrated that their steel (alloy J of Table 3) investigated is capable of producing a low carbon carbide-free bainitic microstructure at 320 °C, and the co-addition of Al and Si in the steel effectively suppresses the precipitation of cementite. They obtained a microstructure consisting of mainly fine lath-shaped bainitic ferrite and thin film-like retained austenite with lower or no amount of martensite. A toughness of 132–152 J/cm², elongation to fracture of 20%, and tensile strength more than 1400 MPa was achieved.

Wang et al. [29] and Long et al. [30] investigated a steel (alloy K, Table 3) with 0.35 wt% C. The measured Ms was found to be 310 °C and accordingly isothermally holding at 320 °C, 330 °C and 380 °C for 1 h was applied to obtain bainite. Raising the transformation temperature resulted in decreasing the

strength from 1450 MPa to 1244 MPa and increasing the ductility from 14% to 17%. The authors adopted different heat treatment techniques similar to that applied in [27] to obtain a wide spectrum of mechanical properties and attaining generations of LTB below Ms of the bulk material.

A study with further increase of C to 0.4 wt% was made by Zhang et al. [31] (alloy L, Table 3). The work-hardening behavior of this alloy was investigated in detail using strain-path reversals to measure the back stresses. It is concluded that the studied material exhibit an extended elasto-plastic transition, as well as a very high kinematic hardening rate which contributes to a very large apparent work-hardening rate. An important result of their study is that the prior austenite grain boundaries are critical for the initiation of fracture due to the absence of carbides. A further study on the topic of “low to medium carbon steel” is carried out by Kharea et al. [25]. They investigated the relative effect of Mo and B on the kinetics of the bainite transformation and hardenability of a carbide free bainite steel with 0.33 wt% C and reported that B, in some circumstances, could accelerate the transformation to allotriomorphic ferrite. No mechanical properties are given in their report.

5. Modifying the processing method

5.1. Continuous cooling

During bainite transformation, a great number of C atoms gradually diffuse from bainite ferrite to the surrounding austenite enriching the untransformed austenite and hence suppressing Ms. During continuous cooling bainite transformation process is expected to take place after coiling during hot rolling operation, allowing the potential comprehensive mechanical properties of the bainitic steel to develop because the finest bainitic plates can be obtained due to the bainitic transformation temperature being lower than conventional single step austempering temperatures. The first work made use of this feature to develop the LTB is reported in [27]. The authors applied different cooling down to 0.03 K/s on alloy I (Table 3) starting from 305 °C (21 °C above Ms). However, in all their studied cooling rates, the bainite transformation process is interrupted by the formation of martensite. Subsequently,

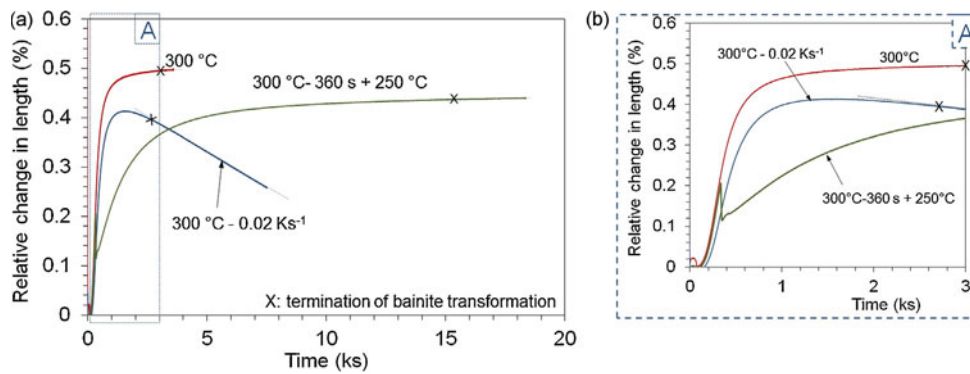


Fig. 4 – Kinetics of bainite formation for different processing techniques applied on alloy F. In (b) details of section A – original.

Wang et al. [29] and Long et al. [30] studied the bainite transformation with continuous cooling from $(M_s + 10)^\circ\text{C}$ to $(M_s - 20)^\circ\text{C}$ within 1 h for alloy K in Table 3 with $M_s = 310^\circ\text{C}$. This composition allowed the bainitic transformation to continue to a great extent without risking the formation of martensite. The authors obtained finer bainitic plate (168 nm) than that obtained by the conventional single step and potentially perfected mechanical properties.

Recently, Das and Halder [32] designed a low carbon steel with 0.34C–1.80Mn–1.51Si–0.92Cr–0.032Ti (wt%). They claimed that this composition delivers a sufficient wide window between M_s and B_s , this helped the bainitic transformation to continue during cooling without being interrupted by the formation of martensite. Thus they were able to produce carbide- and martensite-free steel by continuous cooling from 400°C (5 K above B_s) at a cooling rate of 0.01 K s^{-1} .

5.2. Two-step transformation

The earliest attempt to deviate from the conventional single step bainite transformation was carried out by Papadimitriou and Fournalis [33]. They used a two-stage isothermal heat treatment to generate a bimodal size-distribution of bainite plates. In the context of the LTB, Hase et al. stated that the mechanical properties of this mixture of bainite plates is shown to be better than those of bainite obtained by transformation at any single temperature. They reported an incredible ductility of 40% of total elongation and at an ultimate tensile strength of 1.5 GPa in two stage transformed sample [34].

To allow the formation of generations of bainite below M_s , Soliman et al. [20,27] applied a two-stage isothermal heat treatment in such a way that the first stage is above M_s and the second is below it. During the first stage the untransformed austenite is enriched with carbon that diffused from the formed bainitic ferrite and thus has new martensite start (M_{sII}) which is below M_s . Applying the second transformation stage below M_s but above M_{sII} allowed obtaining a second generation of LTB that is not obtainable in the single stage transformation. More recently, Long et al. [30] and Duong et al. [35] applied the same approach to obtain a generation of bainite formed below the M_s of the bulk material. All the three investigations reported improved strength and ductility for the

two-stage treatment compared with the conventional single-stage one. Further, it is proved that alterations of temperature within the bainite transformation range do not perceptibly affect the reaction rate when compared with isothermal heat treatment [36].

Fig. 4 compares the kinetics of bainite formation in terms of relative change in length (measured using dilatometry) obtained during continuous cooling and two-step techniques with that obtained during the conventional single step isothermal transformation for alloy F. The fast transformation kinetics of alloy F enabled the production of LTB by continuous cooling applying a cooling rate of 0.02 K s^{-1} . Generations of bainite were produced during cooling between 300°C and 246°C (corresponding to 0.75 h of continuous cooling). After bainite formation, the untransformed austenite was enriched with enough carbon that suppressed the martensite transformation during cooling below 246°C . This is indicated from the linearity of the dilatation curve after transformation-termination [37]. It is interesting that the cooling rate of 0.02 K s^{-1} can be easily achieved during the production process of steels, e.g. in stacks of large thick products or in a coiled strip, in which the cooling rates will be sufficiently slow to enable the formation of LTB.

5.3. Thermo-mechanical processing

The deformation behavior of austenite and its effect on M_s in medium-carbon steel, which is designed for the manufacture of LTB steel, were studied by Zhang et al. [38]. In this study, a steel with Fe–0.51C–1.83Mn–1.76Cr–0.51Ni–2.01W–1.26Si–1.51Al (wt%) was subjected to different thermo-mechanical process regimes. Deformation of austenite suppressed M_s decreasing from 294°C of the undeformed austenite to 268°C , 244°C and 228°C of the deformed austenite ($\epsilon = 50\%$) at 900°C , 600°C and 300°C , respectively. The uniaxial compressive stress applied during martensite transformation (the load was kept constant on the specimens after deformation) increased the M_s due to its promotion effect on martensite transformation and lath growth. The strain rate has only a small effect on M_s in the case of a deformation at relatively high temperatures. However, increasing the strain rate decreased the M_s in case of a deformation at lower temperatures. The authors have not published results respecting making use of this effect in

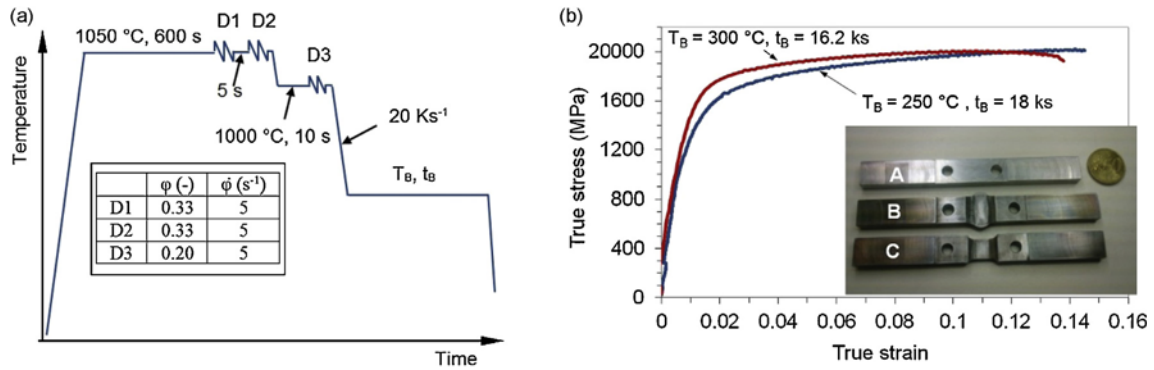


Fig. 5 – Schematic diagram showing the applied thermo-mechanical process. Stress–strain curves of flat-compression specimens before- (A) and after deformation (B) as well as the mini-tensile specimen (C). Alloy (wt.%): 0.56C, 1.66Si, 2.53Mn, 0.25Mo, 1.31Cr, 0.63Al and 1.48Co [39].

producing the LTB in deformed structure (below M_s of the undeformed austenite).

Thermo-mechanically TM processed LTB was produced in a thermo-mechanical simulator through a defined combination of deformation-steps and temperature control. Throughout these experiments, a dilatometry system was used to analyze the transformation kinetics during the TM process [39]. Fig. 5a shows the applied TM schedule. To obtain bainite, the specimens are held at the bainite transformation temperature (T_B) for a certain time (t_B). The time of beginning and end of the corresponding phase transformation were estimated from dilatometric curves. The tensile results presented in Fig. 5b are for a LTB produced in a medium carbon steel with 0.56 wt% C by an isothermal transformation at 300 °C and 250 °C. The tensile results are of samples with non-standard dimensions machined from the TM processed material (designated with (c) in Fig. 5b). Comparing the transformation time of this alloy with that published in [40] for the same alloy but without deformation indicates that the deformation of austenite has a pronounced effect on accelerating the bainite transformation. A further observation of the authors is that deformation also caused a shift of bainite transformation start to very short times leading to a negligible incubation period.

6. Other technological aspects

Some further technological aspects other than the alloying concepts and processing methods are reported for the LTB like:

6.1. Fatigue behavior

The fatigue behavior of the Al-free alloy of Table 1, austempered 200 °C/9 days was investigated by Peet et al. [41]. The tests were performed at high stresses with maximum values between 1.2 GPa and 1.6 GPa. Fatigue limit of ~855 MPa was estimated assuming no failure in 10^7 cycles. Recently, an investigation on rotating bending fatigue behavior of LTB steel was performed on 0.76 wt% C steel microalloyed with vanadium [42]. Fatigue strength has been shown to be increased by reducing the bainitic transformation temperature where fatigue limits were measured to be 820 MPa, 945 MPa,

and 1005 MPa for the samples isothermally transformed at 300 °C, 250 °C, and 200 °C, respectively. They observed that shear strain and secondary crack initiation seem to occur inside the austenite phase for the samples transformed at 300 °C because of a lower C content and lower stability of the austenite in the center of this phase.

6.2. Wear resistance

The dry sliding-friction wear resistance of nanostructured bainite produced in 9SiCr steel has been studied by Wang et al. [43]. They stated that the sliding friction induce the transformation of retained austenite in the top friction surface into carbon-supersaturated α -phase. It is proposed that this strain-induced retained austenite transformation plays an important role in the achievement of extremely fine grains in the top surface layer. The wear resistance of the austempered samples is found to be a little bit higher than that of the quenched and tempered ones of this steel.

On the other hand, the rolling/sliding wear performance of several carbide-free high Si bainitic steels was investigated in the context of rail applications by Yang et al. [16] and Leiro et al. [44]. These nano-structured steels exhibit significantly lower specific wear rates compared to the reference 100Cr6 with lower bainite microstructure and other conventional carbide-free bainitic steels, even at the same hardness levels [16].

6.3. Case hardening

Based on the excellent wear resistance of the low temperature bainitic steel, a novel approach was proposed by Zhang et al. [45,46] for the development of a low-temperature bainitic microstructure in the surface layer of low-carbon steels based on surface carburization and succeeding low-temperature austempering. Because of a potential use of this microstructure in the manufacturing of heavy-duty gears, dry sliding friction was applied to the surface of the resulting microstructure. Case-carburized steel isothermally transformed at 200 °C has been shown to lead to extremely fine and hard bainite (620 HV) in the surface layer, with the transformation inducing a compressive stress of about 200 MPa into the surface. Their

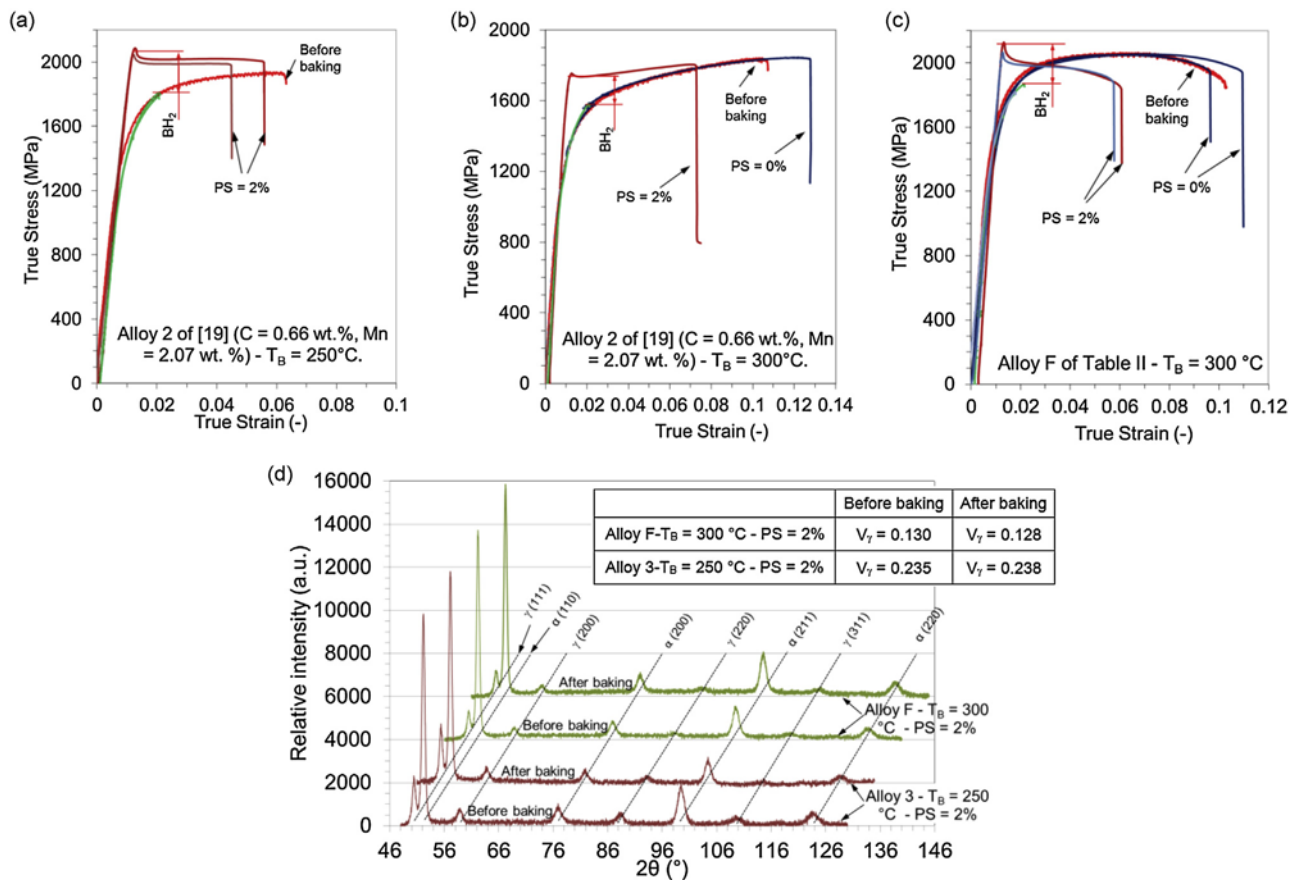


Fig. 6 – (a)–(c) True stress–true strain curves showing the BH_2 effect (baking for 20 min at 170°C) for the prescribed conditions. (d) XRD patterns together with the evaluated retained austenite volume fraction – original.

main conclusion was that at high load, as time of the wear test progresses, the wear rates of the bainitic sample decreased to a lower degree than that martensitic one. The wear rate of the bainitic sample in steady state is less than 80% of the martensitic sample of 20CrMnTi steel subjected to quenching followed by tempering, which is widely used in the area of gears.

6.4. Bake hardening effect

Tests were carried out to investigate the bake hardening (BH) potential of the LTB. The tests were performed on alloy A2 of Ref. [19] with 0.66C–2.17Si–2.07Mn–0.24Mo–1.1Al–1.28Cr–1.70Co (wt%) and on alloy F (Table 2). The samples were baked at 170°C for 20 min after prestraining (PS) with 2% as well as without prestraining (0% PS). Fig. 6 shows the stress strain curves obtained from these tests. In both alloys there is no significant increase in strength for PS = 0. However, a strong effect can be observed applying a PS of 2% before baking (BH_2). This high BH value shifts the yield point to exceed 2 GPa for the cases in Fig. 6a and c. X-ray diffraction (XRD) investigations, see Fig. 6d, illustrate that the BH at 170°C for 20 min has no significant effect on the retained austenite volume fraction (V_γ). This excludes the suspicion of attributing this effect to transformation of retained austenite into martensite during baking. The strong BH effect of this material

can be attributed to its high concentration of carbon atoms in solid solution [47]. Additionally, the nano-structure of the material can cause a strong BH-effect. Raabe and his co-workers [48] concluded that aging at 170°C (bake-hardening) of the ultra-fine grained DP steel ($1.2\ \mu\text{m}$ ferrite grain size) having a YS of 525 MPa leads to a strong increase in YS ($\text{BH}_0 = 94\ \text{MPa}$). The results (Fig. 6) need further experimental investigation [49].

7. Outlook

7.1. Production of low temperature bainite by thermo-mechanical processing

TM processing gives an important alternative for the production of low temperature bainite in which, whilst in the austenite state, the steel is subjected to deformation steps, e.g. by hot rolling or forging. The austenite state can be reached either by heating or possibly immediately after casting from the hot melt. Direct quenching after deformation may limit the quantity of the generated super bainite. Therefore, after deformation, sufficient time should be given for the material to recover and recrystallize. The minimum cooling rate between the austenitization temperature and the bainite transformation temperature to avoid pearlite formation

during cooling should be determined according to the deformation-continuous-cooling-transformation diagram of the material. The low temperature bainite can be formed by isothermal holding for a period of 30 min to 3 days at a temperature between 200 °C and 320 °C. The novel nanostructure bainite can also be formed by continuous cooling transformation, e.g. 0.02 K s⁻¹, if the transformation kinetics is accelerated. This cooling rate can be easily achieved during the production process of steels, e.g. in stacks of large thick products or in a coiled strip, in which the cooling rates will be sufficiently slow to enable the formation of low temperature bainite. This occurs if the cooling from the austenite state reaches the bainite transformation temperature at an appropriate point to allow transformation to low temperature bainite to take place.

7.2. Manganese in low temperature bainite

The known low temperature bainite steel requires a homogenization process (2 days at 1200 °C). The main element that segregates in the structure and requires this process is manganese. Decreasing the manganese decreases the severity of the segregation. Also, manganese reduction is a very effective mean to accelerate bainite formation at low temperatures and increase the quantity of the desired fine bainite. The effect of Mn reduction/removal on the material's hardenability can be counteracted by increasing the content of elements like carbon and molybdenum. However, this element increase can be dispensable in case of heat treating thin-products, where the hardenability diminution can be counteracted by an increased cooling rate.

On the other hand, in case of using high sulfur base metal, a minimum amount of Mn is needed to prevent formation of iron sulfide. Mn is added to steel to a content not less than 0.2 wt%. It actively reacts with iron sulfides during solidification forming ductile manganese sulfides. For high purity base metals with S ≤ 0.002 wt% (solubility of S in Fe at room temperature) Mn can be reduced to zero.

7.3. Processing after bainite formation

The product is considered as a final one, due to its high hardness, machining is allowed only to depth of the decarburized layer (<0.5 mm). This can be considered as a final cleaning process. A modicum of plastic straining (e.g. 2%) on the final product and subsequent baking (e.g. during paint baking) would result in an enormous increase in yield strength, which may exceed 2 GPa. The enormous increase in the yield strength (up to 250 MPa) can be attributed to the bake hardening effect; the suspicion of the contribution of the transformation of retained austenite into martensite during baking is excluded.

Funding

The work done by the authors in this article was financially supported by the Deutsche Forschungsgemeinschaft (DFG) – PA 837/16-1.

REFERENCES

- [1] B.P.J. Sandvik, H.P. Nevalainen, Structure–property relationships in commercial low-alloy bainitic–austenitic steel with high strength, ductility, and toughness, *Materials Science and Technology* 8 (1981) 213–220.
- [2] H.K.D.H. Bhadeshia, D.V. Edmonds, Bainite in silicon steels new composition-property approach Part 1, *Materials Science and Technology* 17 (1983) 411–419.
- [3] F.C. Zhang, B. Lv, C.L. Zheng, Q. Zou, M. Zhang, M. Li, T.S. Wang, Microstructure of the worn surfaces of a bainitic steel railway crossing, *Wear* 268 (2010) 1243–1249.
- [4] J. Mahieu, B.C. De Cooman, S. Claessens, Galvanizability of high-strength steels for automotive applications, *Metallurgical and Materials Transaction A* 32 (11) (2001) 2905–2908.
- [5] P. Pointner, High strength rail steels – the importance of material properties in contact mechanics problems, *Wear* 265 (2008) 1373–1379.
- [6] J. Chakraborty, D. Bhattacharjee, I. Manna, Austempering of bearing steel for improved mechanical properties, *Scripta Materialia* 59 (2008) 247–250.
- [7] E. Kozeschnik, H.K.D.H. Bhadeshia, Influence of silicon on cementite precipitation in steels, *Materials Science and Technology* 24 (2008) 343–347.
- [8] C. Garcia-Mateo, F.G. Caballero, H.K.D.H. Bhadeshia, Development of hard bainite, *ISIJ International* 43 (2003) 1238–1243.
- [9] C. Garcia-Mateo, F.G. Caballero, H.K.D.H. Bhadeshia, Acceleration of low-temperature bainite, *ISIJ International* 43 (2003) 1821–1825.
- [10] F.G. Caballero, H.K.D.H. Bhadeshia, K.J.A. Mawella, D.G. Jones, P. Brown, Very strong low temperature bainite, *Materials Science and Technology* 18 (2002) 279–284.
- [11] F.G. Caballero, H.K.D.H. Bhadeshia, Very strong bainite, *Current Opinion in Solid State and Materials Science* 8 (2004) 251–257.
- [12] F.G. Caballero, H.K.D.H. Bhadeshia, K.J.A. Mawella, D.G. Jones, P. Brown, Design of novel high-strength bainitic steels: Part I, *Materials Science and Technology* 17 (2001) 512–516.
- [13] H.K.D.H. Bhadeshia, Nanostructured bainite, *Proceedings of the Royal Society of London A* 466 (2010) 3–18.
- [14] M.J. Peet, H.K.D.H. Bhadeshia, Surface relief due to bainite transformation at 473 K (200 °C), *Metallurgical and Materials Transaction A* 42 (2011) 3344–3348.
- [15] M.N. Yoozbashi, S. Yazdani, T.S. Wang, Design of a new nanostructured, high-Si bainitic steel with lower cost production, *Materials and Design* 32 (2011) 3248–3253.
- [16] J. Yang, T.S. Wang, B. Zhang, F.C. Zhang, Microstructure and mechanical properties of high-carbon Si–Al-rich steel by low-temperature austempering, *Materials and Design* 35 (2012) 170–174.
- [17] H. Huang, M.Y. Sherif, P.E.J. Rivera-Díaz-del-Castillo, Combinatorial optimization of carbide-free bainitic nanostructures, *Acta Materialia* 61 (2013) 1639–1647.
- [18] US 20110126946 A1, Bainite steel and methods of manufacture thereof, 2 (2011).
- [19] M. Soliman, H. Palkowski, Controlled setting of the transformation kinetics and the structure constituents in low-temperature bainite steels, in: *The Minerals, Metals & Materials Society (Ed.), TMS 2013 Supplemental Proceedings*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2013 901–908.
- [20] M. Soliman, H. Palkowski, Verfahren zum Herstellen eines Bauteils mit bainitischem Gefüge und entsprechendes Bauteil, DE102012017143 B3 (2012).
- [21] H. Amel-Farzad, H.R. Faridi, F. Rajabpour, A. Abolhasani, S. Kazemi, Y. Khaledzadeh, Developing very hard nanostructured

- bainitic steel, *Materials Science & Engineering A* 559 (2013) 68–73.
- [22] H.K.D.H. Bhadeshia, *Bainite in Steels*, Institute of Materials, London, 2001.
- [23] M. Soliman, H. Palkowski, Ultra-fine bainite structure in hypo-eutectoid steels, *ISIJ International* 47 (2007) 1703–1710.
- [24] H.I. Aaronson, H.A. Domian, G.M. Pound, Thermodynamics of the austenite-proeutectoid ferrite transformation: Fe–C alloys, *Transactions of the Metallurgical Society of AIME* 236 (1966) 753–767.
- [25] S. Kharea, K. Leeb, H.K.D.H. Bhadeshia, Relative effects of Mo and B on ferrite and bainite kinetics in strong steels, *International Journal of Materials Research* 100 (2009) 1513–1520.
- [26] H.S. Yang, H.K.D.H. Bhadeshia, Designing low carbon, low temperature bainite, *Materials Science and Technology* 24 (3) (2008) 335–342.
- [27] M. Soliman, H. Mostafa, A.S. El-Sabbagh, H. Palkowski, Low temperature bainite in steel with 0.26 wt% C, *Materials Science & Engineering A* 527 (2010) 7706–7713.
- [28] L. Qian, Q. Zhou, F. Zhang, J. Meng, M. Zhang, Y. Tian, Microstructure and mechanical properties of a low carbon carbide-free bainitic steel co-alloyed with Al and Si, *Materials and Design* 39 (2012) 264–268.
- [29] Y.H. Wang, F.C. Zhang, T.S. Wang, A novel bainitic steel comparable to maraging steel in mechanical properties, *Scripta Materialia* 68 (2013) 763–766.
- [30] X.Y. Long, J. Kang, B. Lv, F.C. Zhang, Carbide-free bainite in medium carbon steel, *Materials and Design* 64 (2014) 237–245.
- [31] X. Zhang, G. Xu, X. Wang, D. Embury, O. Bouaziz, G.R. Purdy, H.S. Zurob, Mechanical behavior of carbide-free medium carbon bainitic steels, *Metallurgical and Materials Transaction A* 45A (3) (2014) 1352–1361.
- [32] S. Das, A. Haldar, Continuously cooled ultrafine bainitic steel with excellent strength–elongation combination, *Metallurgical and Materials Transactions A* 45A (2014) 1844–1854.
- [33] G. Papadimitriou, G. Fourlaris, A TEM investigation of the stepped bainite reaction in silicon steels, *Journal de Physique IV France* 7 (1997), C5-131–C5-136.
- [34] K. Hase, C. Garcia-Mateo, H.K.D.H. Bhadeshia, Bimodal size-distribution of bainite plates, *Materials Science & Engineering A* 438–440 (2006) 145–148.
- [35] V.T. Duong, Y.Y. Song, K.-S. Park, H.K.D.H. Bhadeshia, D.-W. Suh, Austenite in transformation-induced plasticity steel subjected to multiple isothermal heat treatments, *Metallurgical and Materials Transactions A* 45A (2014) 4201–4209.
- [36] H.S. Hasan, M. Peet, H.K.D.H. Bhadeshia, S. Wood, E. Booth, Temperature cycling and the rate of the bainite transformation, *Materials Science and Technology* 26 (4) (2010) 453–456.
- [37] M. Soliman, B. Weidenfeller, H. Palkowski, Metallurgical phenomena during processing of cold rolled TRIP steel, *Steel Research International* 80 (1) (2009) 57–65.
- [38] M. Zhang, Y.H. Wang, C.L. Zheng, F.C. Zhang, T.S. Wang, Austenite deformation behavior and the effect of ausforming process on martensite starting temperature and ausformed martensite microstructure in medium-carbon Si–Al-rich alloy steel, *Materials Science and Technology A596* (2014) 9–14.
- [39] M. Soliman, H. Palkowski, Thermo-mechanische Simulation zur Einstellung mechanischer Eigenschaften des Super-Bainits, *Neuere Entwicklungen in der Massivumformung*, Stuttgart, 2013, pp. 337–341.
- [40] M. Soliman, H. Palkowski, Microstructure development and mechanical properties of medium carbon carbide-free bainite steels, *Procedia Engineering* 81 (2014) 1036–1311.
- [41] M.J. Peet, P. Hill, M. Rawson, S. Wood, H.K.D.H. Bhadeshia, Fatigue of extremely fine bainite, *Materials Science and Technology* 27 (2011) 119–123.
- [42] B.R. Shendy, M.N. Yoozbashi, B. Avishan, S. Yazdani, An investigation on rotating bending fatigue behavior of nanostructured low-temperature bainitic steel, *Acta Metallurgica Sinica (English Letters)* 27 (2014) 233–238.
- [43] T.S. Wang, J. Yang, C.J. Shang, X.Y. Li, B. Lv, M. Zhang, F.C. Zhang, Sliding friction surface microstructure and wear resistance of 9SiCr steel with low-temperature austempering treatment, *Surface and Coatings Technology* 202 (2008) 4036–4040.
- [44] A. Leiro, E. Vuorinen, K.G. Sundin, B. Prakash, T. Sourmail, V. Smanio, G. Caballero, C. Garcia-Mateo, R. Elvira, Wear of nano-structured carbide-free bainitic steels under dry rolling–sliding conditions, *Wear* 298–299 (2013) 42–47.
- [45] F.C. Zhang, T.S. Wang, P. Zhang, C.L. Zheng, B. Lv, M. Zhang, Y.Z. Zheng, Novel method for the development of a low-temperature bainitic microstructure in the surface layer of low-carbon steel, *Scripta Materialia* 59 (2008) 294–296.
- [46] P. Zhang, F.C. Zhang, Z.G. Yan, T.S. Wang, L.H. Qian, Wear property of low-temperature bainite in the surface layer of a carburized low carbon steel, *Wear* 271 (2011) 697–704.
- [47] S. Das, S.B. Singh, O.N. Mohanty, Effect of free carbon and aging condition on bake hardening, *Ironmaking and Steelmaking* 38 (2011) 139–143.
- [48] M. Calcagnotto, Y. Adachi, D. Ponge, D. Raabe, Deformation and fracture mechanisms in fine- and ultrafine-grained ferrite/martensite dual-phase steels and the effect of aging, *Acta Materialia* 59 (2011) 658–670.
- [49] M.Y. Sherif, Characterisation and Development of Nanostructured, Ultrahigh Strength, and Ductile Bainitic Steels, (Ph.D. thesis), University of Cambridge, 2006.