

Article



The Nitrocarburising Response of Low Temperature Bainite Steel

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Abstract: The nitrocarburising response of low transformation temperature ultrafine and nanoscale bainitic steel was investigated and compared with martensite and pearlite from the same steel composition. It was found that the retained austenite content of the bainitic steel dictated the core hardness after nitrocarburising. The refined bainitic structure showed improvements in the nitriding depth and hardness of the nitrocarburised layer, compared to coarser grained martensitic and pearlitic structures, possibly due to the fine structure and the distribution of nitride forming elements.

Keywords: low temperature bainite; nitrocarburising; surface modification; retained austenite; bainitic ferrite; transmission electron microscopy

1. Introduction

Recent developments in the compositional design and thermal treatment of high-strength steels have challenged the traditional compromise between strength and toughness. By refining bainitic ferrite laths to a nanometer scale, a new generation of nanostructured bainite steels have emerged, offering a highly desirable combination of properties: high strength (2.3 GPa), toughness (30 MPa m^{1/2}) and ductility (30%) in both quasistatic and dynamic loading conditions [1–3]. The potential application range of these steels is broad, encompassing the transport, construction and defense industries. In all of these applications, there is potential for improved performance by enhancing the surface properties. There have been studies of microstructure and property relationships [1–4], crystallography [5,6], wear behavior [7,8], and thermal tempering [9,10] of nano-bainitic steels (henceforth termed low temperature bainite) but it has been no attempt to enhance its surface properties.

Ferritic nitrocarburising is a thermo-chemical surface treatment designed to diffuse nitrogen and carbon into the surface of ferrous materials [11]. A surface structure typically consists of a hard outer iron carbonitride (ε -Fe₂₋₃(C, N)_{1-x}) compound layer and a tough inner nitrogen-enriched diffusion zone [11]. The addition of a carbon-bearing gas to the treatment atmosphere distinguishes nitrocarburising from nitriding, and increases the nitrogen diffusion kinetics. Due to the compatibility between the kinetics of compound layer growth and the tempering behavior of the low temperature bainitic steel, nitrocarburising was chosen in preference to nitriding in this study. The growth of both the compound layer and diffusion zone depends on the process conditions (time, temperature, nitriding potential) and nitrogen diffusivity. The latter factor is strongly influenced by the grain structure of the materials. It has been found [12–15] that materials that have a large number of grain boundaries (e.g., an ultrafine or nanocrystalline material) exhibit faster nitriding kinetics, where the grain boundaries act as diffusion channels. Moreover, low temperature bainitic steel exhibits excellent tempering resistance [16], which is beneficial for the nitrocarburasing treatment.

This study explores the nitrocarburising response of the low temperature bainitic steel and compares this response to coarser structures (martensite and pearlite) of the same material composition.

2. Materials and Methods

The steel composition used in this study (0.79C-1.5Si-1.98Mn-0.98Cr-0.24Mo-1.06Al-1.58Co wt %) was based on a composition proposed in [1]. To form low temperature bainite, the steel was austenitized at 1100 °C for 30 min, followed immediately by an isothermal heat treatment between the M_s (155 °C) and B_s (385 °C) temperatures. The starting bainite (B_s) and martensite (M_s) phase transformation temperatures were chosen to be 385 and 155 °C, respectively, based on previously published work [17]. Two isothermal treatments were used; 200 °C for 10 days ('200' bainite) and 350 °C for 1 day ('350' bainite) [6]. The air and furnace cooling from the austenitizing temperature were used to form martensite ('M') and coarse pearlite ('P'), respectively.

Tempering of the bainitic steels was performed in an air furnace for various times (10–7200 min) and temperatures (250–600 °C), and the resulting core hardness determined by Vickers indention using a 20 kg load and a 10 s dwell time. The tempering response of the bainitic steels was used to determine the nitrocarburising parameters, as will be discussed later. Samples were surface polished (1200 grade SiC), ultrasonically cleaned in ethanol and nitrocarburised in a fluid bed reactor at 525 °C for 4 h in a gaseous atmosphere of 45% ammonia, 3% CO₂ and balance nitrogen. The microstructure of the core and nitrocarburised region was observed by light optical microscopy, and detailed microstructural features were determined by Transmission Electron Microscopy (TEM).

TEM foils, discs 3 mm in diameter, were mechanically ground to a thickness of ~0.07 mm and then twin-jet electropolished using a solution containing 5% perchloric acid and 95% methanol at a temperature of -25 °C and a voltage of 50 V. TEM examination of thin foils was performed using a Philips CM 20 microscope (Philips, Electronic Instruments Corporation, Mahwah, NJ, USA) operated at 200 kV.

The retained austenite volume fractions in the core material after nitrocarburising treatment were determined using a Phillips PW 1130 diffractometer with graphite monochromated CuK_{α} radiation at 40 kV and 25 mA in the 2 θ range of 40–90° at a rate of 0.5°/min and a step size of 0.05° (Philips, Electronic Instruments Corporation, Mahwah, NJ, USA). A Sietronics X-Ray Diffraction (XRD) automation system was used for data collection, with analysis by XRD Traces V. 5.2 software (5.2, GBC Scientific Equipment, Hampshire, IL, USA). The retained austenite content was calculated from the integrated intensities of the (200)_{α}, (211)_{α}, (200)_{γ} and (220)_{γ} peaks using the direct comparison method [18]. Micro-Vickers hardness profiles of the nitrocarburised surfaces were performed on a mounted cross-section using a 50 gf load and a 10 s dwell time. A quantitative depth profile for nitrogen content was obtained using a Leco GDS850 glow discharge optical emission spectrometer (LECO Corporation, Saint Joseph, MI, USA).

3. Results and Discussion

3.1. Characterization of Initial Micostructures

A detailed study of the microstructural characteristics and crystallographic analysis of the low temperature bainite formed at 200 and 350 °C has been reported in [4–6]. Isothermal treatment at 200 °C produced a fine lamella microstructure of alternating films of austenite ($21 \pm 2\%$ vol. fraction, 30 ± 5 nm thick) and bainitic ferrite (60 ± 10 nm thick). The bainitic ferrite and retained austenite layers formed colonies or sheaves, where the layers or sub-units consisting of bainitic ferrite and residual austenite are parallel to each other (Figure 1a).

Increasing the isothermal treatment to 350 °C resulted in formation of bainite packets consisting of nanolayers of bainitic ferrite with thickness from 200 to 400 nm, and retained austenite layers with an average thickness of 70 ± 30 nm (Figure 1b). The bainite/retained austenite sub-unit formed at this temperature was coarser than the similar sub-unit after isothermal holding at 200 °C. The volume fraction of austenite was $53 \pm 1\%$.



Figure 1. TEM (Transmission Electron Microscopy) micrographs of the microstructure formed after 200 $^{\circ}$ C (**a**) and 350 $^{\circ}$ C (**b**) isothermal treatment. RA is retained austenite and BF is bainitic ferrite.

The microstructure of the air-cooled specimen contained both plate and lath martensite morphology in approximately equal proportions (Figure 2a,b). Plate martensite was previously described as plates having a thickness of several microns and a length of tens of microns without further structural subdivisions of these plates (Figure 2a) [19]. In contrast, lath martensite forms the same three-level hierarchy as the bainitic steels, ultimately forming laths of martensite with sub-micrometer thickness (Figure 2b) [20]. The furnace cooled structure was coarse pearlite. The core hardness of each microstructural variant was 380 ± 6 ('350'), 675 ± 7 ('200'), 365 ± 7 ('P') and 654 ± 5 ('M') HV_{50gf}.



Figure 2. TEM images of plate (a) and lath (b) martensite.

3.2. Effect of Tempering on Microstructure and Properties

The tempering behavior is very different for the two bainitic steel variants (Figure 3). A reduction in hardness with time and temperature occurred during the tempering of '200' bainite. In contrast, the '350' bainite exhibited a hardening peak, which occurred earlier with increased tempering temperature. A nitrocarburising process window is indicated in Figure 3. This window provided a balance between favorable nitrocarburising parameters and retaining core hardness.



Figure 3. The hardness response of the '200' (B1) and '350' (B2) bainitic steels during isothermal tempering at various times and temperatures. A nitrocarburising time-temperature process window is indicated.

The retained austenite content of the '200' bainite core reduced from $21 \pm 2\%$ to $12 \pm 1\%$ after nitrocarburising at 525 °C for 4 h. TEM imaging revealed several microstructural features: (i) the lamellar structure was largely retained, (ii) spherical cementite particles (10–50 nm diameters) formed within the bainitic ferrite (Figure 4a,b), (iii) the dislocation density of the bainitic ferrite decreased, and (iv) some of the retained austenite films decomposed with formation of cementite (Figure 4a,b). Our recent study of the initial microstructure of similar steels under similar isothermal conditions using TEM and Atom Probe Tomography showed [4] a high volume fraction of clusters and carbides in bainitic ferrite, and low stability of the retained austenite. This was associated with high dislocation density in bainitic ferrite and preferential segregation of carbon to the dislocations in ferrite rather than diffusing to the remaining austenite [4]. Tempering of this microstructure promoted the fast carbon diffusion that led to the formation of spherical carbides in bainitic ferrite and decomposition of the retained austenite with carbon. Hence, the general decrease in hardness with time and temperature for the '200' bainite is reasonable.

In contrast, the '350' bainite experienced significant core hardening of nearly 200 HV after nitrocarburising at 525 °C for 4 h (Figure 3). Certainly, the hardness increase is related to the large decrease in retained austenite from $53 \pm 1\%$ to $4 \pm 1\%$. The austenite decomposed to form carbides of lenticular morphology with a width of ~10 nm (Figure 4c). TEM also confirmed the formation of spherical carbides in the bainitic ferrite (Figure 4d). Other studies [9,10] have shown that blocky austenite in nanostructured bainite can form pearlite with an extremely fine lamellar spacing when tempered above 500 °C. It would appear that the thicker initial austenite films in the '350' bainite decompose in a similar manner to blocky austenite. The conversion of half of the structure from austenite to extremely fine pearlite during nitrocarburising could account for the hardening. Another possibility is that the austenite has decomposed to a mixture of ferrite and lenticular carbides. The nitrocarburising could result in an increase in the M_s temperature in the retained austenite films, leading to martensite transformation. This would give a large increase in hardness. At this stage, though, it is not clear exactly what mechanism is responsible, but the important issue here is that it is possible to obtain a high core strength in the '350' bainite.

The decomposition of the retained austenite with an increase in tempering temperature has been reported in [9,10]. However, it is still unclear how the ferrite component can accommodate the extremely high quantity of carbon during retained austenite decomposition.



Figure 4. Bright (**a**,**c**) and dark (**b**,**d**) TEM images of the bainite core microstructure formed after nitrocarburising at 525 °C for 4 h in '200' (**a**,**b**) and '350' (**c**,**d**) bainite: (**a**,**b**) formation of spherical carbides in bainitic ferrite (dark arrows) and decomposition of retained austenite (white arrows), (**c**) decomposition of the retained austenite with formation of lenticular carbides (white arrow) and (**d**) spherical carbides in the bainitic ferrite.

00nm

(c)

After nitrocarburising the core hardness was highest in the bainitic steels at 578 \pm 8 and 542 \pm 4 HV_{50gf} for the 350 and 200 °C isothermally treated variants, respectively (Figure 3). The core hardness of the martensitic steel was 514 \pm 4 HV_{50gf} and the core hardness of the pearlitic steel was 369 \pm 9 HV_{50gf}. This demonstrates the good tempering resistance of the nanobainitic steels, a property that Cabellero [10] has attributed to the complex partitioning and microstructural changes that occur during reheating. High core hardness is desirable for a nitrocarburised component, as it provides good core strength and load carrying capacity. If core hardness and strength are desired, then low temperature bainite is an appropriate starting material. From a processing standpoint, it is significant that the '350' variant produced the higher core hardness, as the treatment time is shorter by a factor of 10. However, other mechanical properties are also significant, notably ductility and toughness, which may benefit from the higher level of retained austenite present in the '200' variant. A worthwhile extension of this work would be to examine the effect of tempering on other mechanical properties.

A compound layer and diffusion zone formed on all material variants (see micrographs in Figure 5a–d). The compound layers were similar in thickness and nitrogen concentration for all

100nm

(d)

microstructures; however, the total nitrogen diffusion depth and concentration varied. The bainitic steel produced diffusion zones with higher nitrogen content and increased depth relative to the martensitic and pearlitic variants (Figure 5). These increased nitrogen levels and depths were reflected in the hardness profiles (Figure 5). It is evident from the very high hardness achieved (>1300 HV) in the compound layer and adjacent diffusion zone that the composition of this bainitic steel is appropriate as a nitrocarburising steel.



Figure 5. Nitrocarburised microstructures of (**a**) '200' bainite (B1), (**b**) '350' bainite (B2), (**c**) 'M' (**d**) 'P' and (**e**) quantitative depth profiles of nitrogen and hardness profiles in the nitrocarburised surface of all the microstructural variants.

The variations in diffusion depth and hardness may be related to the microstructures. Materials subjected to surface nanocrystallisation processes [13–15] have shown substantially increased nitrogen diffusion rates and kinetics of compound layer formation in nitriding processes. Here grain boundaries act as diffusion channels, as the diffusion rate of nitrogen at grain boundaries is twice that of the matrix [15]. The improved diffusion depth in nanostructured bainitic steel, compared to plate/lathe martensitic and coarse pearlitic steel, may be a result of the finer grain structure.

The hardness achieved in the compound layer and diffusion zone of nitrocarburised steels depends on the precipitation of fine-scale alloy nitrides. The most effective substitutional solutes are aluminium and chromium, which form CrN, Cr₂N and AlN precipitates. The higher diffusion zone nitrogen content and hardening in the nanobainitic steel compared to martensitic and pearlitic may be related to solute (Cr, Al) distribution. The partitioning of solute elements in nanostructured bainite during tempering has been characterized by using APT [10]. Below 500 °C, there is negligible solute redistribution across phase boundaries. Above 500 °C, there is enhanced redistribution of chromium around precipitated cementite, where the levels attained approach partitioning local equilibrium (7.20 at. % Cr). Chromium mobility is required for precipitate formation, so this observed segregation of chromium is of interest to the nitrocarburising process. Tong et al. [15] have found in surface nanocrystallized lath martensitic steel that Cr₂N formed near the surface during nitriding at 400 °C, which is 150 °C lower than the typical formation temperature in coarser grained martensite, and was related to the short distance required for solutes to diffuse. It is possible that the solute diffusion distances required to form alloy nitrides is reduced in the low temperature bainite, resulting in a finer

dispersion of alloy nitrides. APT analysis of solute distribution in the diffusion zone of nanobainite structures is required to confirm this.

4. Conclusions

Two low transformation temperature ultrafine and nanostructured bainites, a martensitic and a pearlitic microstructural variant of a steel with the composition 0.79C-1.5Si-1.98Mn-0.98Cr-0.24Mo-1.06Al-1.58Co wt % were studied for their nitrocarburising response. After the nitrocarburising process, the core hardness of the bainitic steels was related to the amount of retained austenite in the starting microstructure. The significant core hardening experienced by the 350 °C isothermally treated steel appears to be the result of lenticular cementite precipitation in the retained austenite lath and block structure. The ultrafine or nano-scale bainitic structure is particularly suitable for nitrocarburising treatment showing good tempering resistance of the core. Additionally this structure may have assisted the diffusion of nitrogen to produce deeper nitrogen diffusion zones. Generally hardness was increased in the nitrided low temperature bainitic structure potentially as a result of the reduced diffusion distances required to form a fine dispersion of alloy nitrides.

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