Generating duplex microstructures by nitriding; nitriding of iron based Fe–Mn alloy

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Nitriding of Fe–2 at-%Mn alloy at 650°C employing a nitriding potential of 0.05 atm$^{-1/2}$ resulted in a highly complex microstructural development as a function of depth below the specimen surface: a surface adjacent layer exhibiting an austenite–martensite duplex microstructure, followed by an intermediate region showing a ferrite–austenite duplex microstructure, and at even larger depths a region where an austenite layer covers the grain boundaries of the ferrite matrix grains. Development of this complex microstructure is attributed to the strong austenite stabilising effects of Mn and N. This work demonstrates the power of a relatively simple nitriding treatment to realise a highly complex microstructure known to be associated with strongly enhanced mechanical properties.

Keywords: Fe–Mn alloy, Nitriding, Duplex microstructure, Austenite–ferrite, Austenite–martensite

Introduction

Enhancement of surface properties of engineering components by thermochemical surface treatments is common practice in industry.1–2 Gaseous nitriding likely is the most widely employed thermochemical surface treatment by which tremendous improvement of the wear, fatigue and/or corrosion resistances of steel components can be realised.1,3 Prediction and optimisation of the developing microstructures, and thus the resulting properties, of steel components upon nitriding require fundamental knowledge on (i) the interaction of inwardly diffusing interstitial nitrogen and the substitutionally dissolved alloying elements of the steel substrate and (ii) the effect of dissolved alloying elements and/or the already developed alloying element nitride particles in the ferrite matrix on the nucleation and growth of iron nitrides and iron–nitrogen austenite.

Fundamental nitriding studies have been carried out on relatively simple model binary and ternary iron based ferritic alloys, which led to the understanding of the basics of the thermodynamics and kinetics of the development of alloying element nitrides in ferrite.3–8 In addition, the influence of alloying elements on the developing iron nitride layers on ferritic steel substrates has been investigated extensively.9–12 The growth of iron–nitrogen (expanded) austenite layers on austenitic steel substrates has been studied.1,13–16 However, the role of alloying elements in the steel matrix as potentially influencing the resulting nitrided microstructure, in a dramatic way, by a change of the crystal structure of the nitrided matrix, has not received distinct attention until now.

It will be shown in the present paper that the alloying element Mn, dissolved in the originally ferritic matrix, upon nitriding can give rise to the development of austenite–ferrite and austenite–martensite duplex microstructures. Such duplex microstructures are known to exhibit a desirable combination of properties.17–19 An Fe–2 at-%Mn alloy was chosen as model system, also in view of the usage of Mn as an austenite stabiliser in many commercial steels. Controlled gaseous nitriding experiments, i.e. at fixed chemical potential of nitrogen, were carried out. The resulting microstructures were characterised by light microscopy (LM), scanning electron microscopy, transmission electron microscopy, X-ray and electron backscatter diffraction (EBSD) and electron probe microanalysis (EPMA). A discussion based on interpretation of the obtained results is presented.

Experimental

Specimen preparation and nitriding

Fe–2 at-%Mn alloy was prepared from elemental Fe with a purity of 99.98 wt-%, and elemental Mn with a purity of 99.999 wt-% by melting in an inductive furnace under protective argon atmosphere. The alloy melts were cast into rectangular moulds of dimensions 80 × 12 × 13 mm$^3$. The ingots were cut into two pieces and encapsulated in a quartz tube filled with argon gas.

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Such encapsulated cast pieces were annealed at 1000°C for 1 h to achieve chemical homogeneity. The annealed cast pieces were then cold rolled to sheets of ~1-0 mm thickness. From these sheets, rectangular specimens (20 mm × 15 mm) were cut. After grinding and polishing (finishing with 1 μm diamond paste) of the surfaces of the specimens, the specimens were encapsulated in a quartz tube filled with argon and recrystallised at 700°C for 1 h. Results of chemical analysis of the cast material are presented in Table 1; metal contents were determined by inductively coupled plasma optical emission spectroscopy, light element contents (N and O) were determined by carrier gas hot extraction and the C content was determined by a combustion method.

The specimens were nitrided in a laboratory scale, vertical quartz tube furnace having an inner diameter of 28 mm, equipped with a facility to suspend the specimen in the middle of the furnace and a water quenching flask, to quench the specimens after completion of the nitriding treatment. For the nitriding treatment, high purity ammonia (99.99 vol.-%) and hydrogen (99.99 vol.-%) gases were used. Before starting the nitriding treatment, the furnace was purged with nitrogen gas to remove all oxygen and other gases adsorbed at the furnace walls. The flowrates of the ammonia (25 mL min⁻¹) and hydrogen (475 mL min⁻¹) gases were set by MKS mass flow controllers to establish a nitriding potential rₙ of 0.05 atm⁻¹/₂. The total gas flowrate of 500 mL min⁻¹ corresponds with a linear gas velocity of 13.5 mm s⁻¹, at room temperature. The specimen was suspended in the uniform temperature (650°C) zone of the furnace with the help of a quartz fibre. At the applied potential nitrogen partial pressure at the surface and decreases to ~0.02 atm⁻¹/₂ at 20–120°, with a step size of 0-2° (20) and with a counting time of 200 s per step.

Transmission electron microscopy (TEM) was carried out for characterisation of the nanosized nitride precipitates. To obtain electron transparent foils, nitrided specimens were ground from both sides (faces) until the desired location of the nitrided region (i.e. depth in the nitrided zone and parallel to the surface of the specimen). Then, discs of 3 mm diameter were punched out mechanically and subsequently thinned by ion milling applying the PIPS (Gatan precision ion polishing system) at an accelerating voltage of 3–4 kV, a current of 10–12 μA, an incidence angle of 8° and a milling time of 4–10 h. The TEM analysis was performed using a Philips CM 200 transmission electron microscope operated at 200 kV. Bright field (BF) images, dark field images and selected area diffraction patterns (SADPs) were recorded using a Gatan charge coupled device camera.

**Results**

The LM images, EBSD phase maps and EPMA elemental (Mn and N) concentration–depth profiles recorded from the cross-section of a nitrided (650°C, 20 h, rₙ = 0.05 atm⁻¹/₂) Fe–2 at-%Mn alloy specimen reveal the following distinct microstructures as a function of depth (Figs. 1 and 2): (i) Surface adjacent region; austenite (γ)–martensite (α′) duplex microstructure: This region, appearing as a layer in the LM image (Fig. 1a), actually consists of a mixture of strained body-centred cubic (BCC) phase (α′ = martensite; see caption of Fig. 1b) and face-centred cubic (FCC) phase, as demonstrated by the EBSD analysis (Fig. 1b). Both phases in this region contain a nearly constant and same amount of Mn (~1-8 at-%). The nitrogen content is ~6-5 at-% at the surface and decreases to ~6 at-% at the bottom of this surface adjacent layer (Fig. 2). As the nitrogen solubility in BCC iron can attain a value of maximally ~0-4 at-%, the strained BCC phase must

![Table 1 Composition of the cast Fe–2 at.%Mn alloy (balance Fe)](image)

| Mn/wt-%  | Mn/at.%  | O/wt-%  | N/wt-%  | C/wt-%  |
|----------|----------|---------|---------|---------|
| 1.92 ± 0.02 | 1.95 ± 0.03 | 0.0025 ± 0.0007 | <0.001 | 0.0033 ± 0.0004 |
have been FCC (Fe–N–Mn) austenite (c) at the nitriding temperature and at the applied nitriding potential, which, upon water quenching of the specimen, from nitriding temperature to room temperature, must have transformed to BCT (Fe–N–Mn) martensite. The X-ray diffraction pattern recorded from the surface of the nitrided specimen confirmed the existence of austenite and martensite phases in the surface adjacent region (see Fig. 3). Hence, the surface adjacent region consists of an austenite–martensite duplex microstructure.

(ii) Intermediate region; austenite (c)–ferrite (a) duplex microstructure: This region shows a microstructure composed of particles of FCC crystal structure embedded in a BCC matrix (Fig. 1b). The FCC (second phase) particles are enriched with Mn and N as compared to the surrounding BCC matrix (Fig. 2), which contains less Mn than the unreacted substrate. Hence, the intermediate region consists of a ferrite–austenite duplex microstructure.

(ii) Deepest nitrided region; austenite (γ) grain boundary phase: This region exhibits a layer of second phase at the grain boundaries of the ferrite matrix (Fig. 1a), which, according to the EBSD analysis, is of FCC crystal structure (Fig. 1b) and, according to the EPMA analysis (Fig. 2), enriched with Mn and N. Hence, this deepest nitrided region consists of ferrite matrix grains enveloped by thin layers of austenite along the grain boundaries.
High magnification SEM images recorded from the intermediate region (Fig. 4a) and deepest nitrided regions (Fig. 4b) reveal the presence of fine platelet type and globular type second phase particles in the ferrite matrix. The TEM analysis revealed that the thin platelet type nitrides are of FCC Mn$_4$N type\(^{23}\) with their broad faces parallel to \{001\} lattice planes of the ferrite matrix and exhibiting a Baker-Nutting\(^{24}\) orientation relationship between the FCC type Mn$_4$N platelets and the BCC ferrite matrix (Fig. 5). The TEM analysis of the globular type nitrides showed these to be of orthorhombic Mn$_2$N$_{0.86}$ type\(^{25}\) (Fig. 6; note that the orthorhombic crystal structure for this nitride can be a consequence from cooling below 0°C during ion milling for TEM foil preparation, as it has been reported that a hexagonal→orthorhombic transformation can occur upon cooling to subzero temperature\(^{25}\)). The austenite regions in the duplex austenite + martensite and austenite + ferrite microstructures and the martensite regions in the duplex austenite + martensite microstructure do not contain Mn nitride precipitates.

**Discussion**

Upon nitriding a pure iron specimen at the same nitriding conditions as used in this present work for Fe–2 at-%Mn alloy ($T = 650$ °C and $r_N = 0.05$ atm\(^{1/2}\)) only an Fe–N ferrite (solid solution) develops.\(^{20,26}\) Indeed, the employed nitriding conditions of $r_N = 0.05$ atm\(^{1/2}\) and $T = 650$°C are within the $\alpha$-Fe region of the Lehrer diagram,\(^{20,21}\) but they are near to the $\alpha$-Fe/$\gamma$-Fe phase boundary, suggesting that the occurrence of

![X-ray diffraction pattern (Co K$_\alpha$) recorded from surface of Fe–2 at-%Mn alloy specimen nitrided at 650°C for 20 h using nitriding potential of 0.05 atm\(^{1/2}\). Surface adjacent region contains austenite and martensite phases](image)

![TEM BF image showing the Mn nitride platelets oriented with their broad faces parallel to the 001 lattice planes of the ferrite matrix. TEM foil was prepared from ~75 μm below the surface (i.e. intermediate region) of Fe–2 at-%Mn specimen nitrided at 650°C for 20 h using a nitriding potential of 0.05 atm\(^{1/2}\).](image)

![a TEM BF image showing the Mn nitride platelets oriented with their broad faces parallel to the 001 lattice planes of the ferrite matrix. TEM foil was prepared from ~75 μm below the surface (i.e. intermediate region) of Fe–2 at-%Mn specimen nitrided at 650°C for 20 h using a nitriding potential of 0.05 atm\(^{1/2}\).](image)

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austenite in nitrided Fe–Mn alloy can be caused by a slight shift of the \( \alpha\)-Fe/\( c\)-Fe phase boundary towards lower nitriding potentials and/or temperatures due to the presence of (austenite stabilising) Mn. Even a nitriding experiment performed in this present work with the same Fe–Mn alloy specimen at a much reduced nitriding potential of 0.02 atm \( ^{1/2} \) at the same temperature (650°C) did already result in the formation of austenite, in particular along the ferrite grain boundaries. This finding indicates the strong promotion of austenite stability by dissolved Mn.

The interesting variation of the (duplex) microstructure that developed as a function of depth is compatible with the corresponding isothermal section of the ternary Fe–Mn–N phase diagram at 650°C and at 1 atm as predicted employing the CALPHAD approach.\(^{27}\) Upon introducing nitrogen at 650°C into the initially ferritic (\( \alpha \)) Fe–2 at-%Mn alloy, the following phase sequence is expected to develop as a function of increasing nitrogen content: two phase (\( \alpha + \text{Mn}_6\text{N}_8 \))→three phase (\( \alpha + \gamma + \text{Mn}_6\text{N}_8 \))→two phase (\( \alpha + \gamma \))→ single phase \( \gamma \) (see Fig. 7; dashed line). In reverse order, this sequence shows the predicted phases as a function of depth. This prediction largely agrees with the experimental findings of this study. The occurrence of the (for these conditions) metastable Mn\(_4\)N type\(^ {23} \) and Mn\(_2\)N\(_{0.86}\) type\(^ {25} \) nitrides can be a consequence of small differences in the Gibbs energies of formation of these nitrides (per mole Mn; an extensive series of Mn nitrides, with some of which showing polymorphic transformation, has been reported\(^ {25,28–32} \)), so that kinetic reasons may favour the development of metastable nitrides.

At the three phase equilibrium (\( \alpha + \gamma + \text{Mn}_6\text{N}_8 \)), the predicted Mn content of the \( \alpha \) and \( \gamma \) phases is 0-2 at-% and 2-25 at-% respectively, which indicates that during nitriding, a redistribution (between ferrite and austenite) of Mn must occur to nucleate and grow the austenite in ferrite (the initial Mn content of the binary, ferritic Fe–Mn alloy is 2 at-%). Therefore, it is predicted that during the ferrite→austenite transformation upon (continued) nitriding, the Mn nitrides, which had initially developed in the ferrite matrix, dissociate into Mn and N, which get

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6 a transmission electron microscopy BF image showing globular Mn nitride particle in ferrite matrix and corresponding SADP. b 132 and 241 diffraction spots of orthorhombic Mn\(_2\)N\(_{0.86}\) could be identified.\(^ {25} \) Transmission electron microscopy foil was prepared from specimen at depth of ~400 \( \mu \)m below surface (i.e. deepest nitrided region; cf. Figure 4b) of Fe–2 at-%Mn specimen nitrided at 650°C for 20 h using a nitriding potential of 0.05 atm \( ^{1/2} \). c dark field image formed using 132 diffraction spot of Mn\(_2\)N\(_{0.86}\), illuminating globular Mn\(_2\)N\(_{0.86}\) particle.
dissolved in the developing austenite, which is in agreement with the experimental observation of this study (cf. end of section 3).

Apparently, upon increasing N content, the first austenite to develop nucleates at the ferrite grain boundaries [see region (iii)]. Nucleation barriers are smaller at grain boundaries, as grain boundary energy gets released upon nucleation.\(^{33}\) Moreover, segregation at grain boundaries of possibly Mn may promote first development of austenite there too (Mn is an austenite stabilising element\(^{34}\)). As a next stage, and accompanied by a continuous increase in the N content, austenite develops also within the ferrite matrix grains [region (ii)], in association with dissolution of the Mn nitrides, developed before, leading to a completely austenitic region [at the nitriding temperature; region (i)].

The martensite start temperature \(M_s\) of pure iron–nitrogen austenite decreases with increasing content of dissolved N; for the amount of dissolved N larger than 8.5 at-%, the \(M_s\) temperature is beneath room temperature.\(^{35}-37\) Hence, an austenite–martensite duplex microstructure can develop, upon quenching from the nitriding temperature to room temperature, if the maximal amount of dissolved N in the austenitic surface adjacent region of a nitrided pure iron specimen is smaller than 8.5 at-%\(^{38}\); the local amount of retained austenite then depends on the local N content that controls the local \(M_s\) temperature (note that the martensite finish temperature \(M_f\) for pure iron–nitrogen austenite is already below room temperature for dissolved N contents > 2.7 at-%\(^{35}\)). The additional presence of dissolved Mn in the austenitic nitrided surface adjacent region is an additional component, but much less effective than N,\(^{34}\) reducing the \(M_f\) temperature. Evidently, the presence of about 6–6.5 at-% dissolved N and \(\sim 2\) at-% dissolved Mn corresponds with an \(M_f\) temperature well above room temperature (cf. Figures 1–3), so that the duplex austenite–martensite microstructure can develop upon quenching after nitriding. The austenite in the austenite + ferrite region (ii) apparently does not experience a martensitic transformation upon quenching of the specimen from the nitriding temperature (cf. Figure 1b), although its N content is lower than that of the austenite present, at the nitriding temperature, in region (i), which by itself would cause an (even) higher \(M_s\) temperature for the austenite in region (ii) than for the austenite in region (i) (cf. above discussion). The stabilisation of austenite in region (ii) may be a consequence of an effective cooling rate naturally lower in the deeper region (ii) as compared to that experienced by the surface adjacent region (i), in combination with slow decomposition kinetics of this austenite with respect to that experienced cooling rate (note that the substitutionally dissolved Mn, as compared to the interstitially dissolved N, diffuses relatively slowly). Further, the ferrite matrix surrounding the austenite in region (ii) is strengthened by the precipitated Mn nitrides and thereby can hinder accommodation of the volume expansion that is associated with the austenite to martensite transformation.

The austenite–ferrite and austenite–martensite duplex microstructures as developed in this present work are separately known to significantly improve the mechanical properties of engineering components.\(^{17,18}\) Thereby, this work demonstrates that a relatively simple gaseous nitriding treatment allows realising such a technologically promising microstructure, which may lead to future, new applications of the nitriding process.

### Conclusions

Nitriding of Fe–2 at-%Mn alloy at 650°C and at a nitriding potential of 0.05 atm\(^{-1/2}\) generates a complex microstructure as a function of depth:

(i) surface region: austenite–martensite duplex microstructure
(ii) intermediate region: austenite–martensite duplex microstructure
(iii) deepest nitried region: ferrite–martensite microstructure

Upon nitriding, initially Mn nitrides (Mn\(_4\)N type and Mn\(_3\)N\(_{0.86}\) type) develop in the ferrite matrix grains. A ferrite→austenite transformation occurs, likely initially at the ferrite grain boundaries, upon continued nitriding with simultaneous dissolution of Mn nitrides already developed in the ferrite matrix; the Mn and N released are taken up in the developing austenite.

The sequence of phases developing as a function of depth is largely compatible with the ternary Fe–Mn–N phase diagram.

The generated duplex microstructures suggest a new field of application of the nitriding process.

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