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Abstract. This study investigates the effect of N diffusion on a Nb-microalloyed steel made by twin roll casting at 525° C in a KNO_3 salt bath. Nitriding up to 4 h increases the yield strength of the steel by ~50% with only a small drop in ductility, while 6 hours of nitriding causes brittle fracture. The improved mechanical performance after 4 hours of nitriding is thought to be a combined effect of solid solution strengthening of N diffusion and dispersion strengthening from extremely fine Nb-rich precipitates. Coarse features along grain boundaries consistently observed in steel nitrided for 6 hours are considered to be responsible for brittle fracture in samples nitrided for longer.

Introduction

The CASTRIP® process is a revolutionary new twin-rolling method of producing thin steel strip directly from liquid state [1]. Using this technique, thin strip steel can be produced with significantly less energy, time and floor space in comparison to conventional slab casting techniques [1, 2]. Twin roll casting using the CASTRIP® process has enabled development of both plain C steel and Nb-microalloyed steel with unique compositions and physical properties. For example, as-received 0.084 wt% Nb-microalloyed low C steel has been produced having a yield strength of 475 MPa with 14% total elongation in about 1.2mm thin strip.

Previous studies have shown that with developed compositions, Nb atoms stay in the matrix as a solid solution with the relatively fast cooling rate that can be achieved with twin roll casting [3]. C and N contents in these steel compositions are quite low (0.031 and 0.007 wt% respectively). Since the thickness of the as-hot-rolled steel sheets is typically only about 1.0-1.5 mm, rapid diffusion of N into the steel composition is possible. It was found that the hardness of Nb-microalloyed steel can be further increased by nitriding using KNO_3 salt bath heat treatments.

KNO_3 starts to decompose at about 500°C into K_2O, O_2 and N_2. This N_2 is then available to diffuse into steel. Nitriding of interstitial free steel in KNO_3 is believed to increase the yield strength of steels substantially via solid solution strengthening at the expense of ductility. Higher temperature nitriding at 650°C is believed to encourage Fe nitride precipitation mainly at grain boundaries and partly within grains [4-6]. The aim of this study is to investigate the nitriding behavior of a Nb-microalloyed steel made by twin roll casting using a combination of mechanical testing and advanced microscopy.

Materials and Methods

Nitriding was performed on a 1.1mm thick 0.084 wt% Nb-microalloyed steel (Nb-steel) made by twin roll casting with the processing parameters and chemical composition are listed in Table 1. Steel coupons were heated in a KNO_3 salt bath at 525°C, followed by water quenching. LECO combustion analysis was undertaken to determine the N concentration in all samples. For comparison, a 1.1mm Nb-free steel also made by twin roll casting was nitrided, and a N-free heat treatment (achieved by wrapping steel coupons in Al foil) was also carried out on the Nb-steel. The yield strength (YS), ultimate tensile strength (UTS) and total elongation (TE) for each specimen were obtained using standard tensile testing. Hardness was measured using a Vickers micro-hardness indenter with a load of 5kg for the surface measurements and 1kg for the through thickness measurements.

Table 1 Processing parameters and chemical composition (wt. %) of the Nb-free and Nb-microalloyed steels.

Specimen	HR temp (°C)	Coil temp (°C)	thickness (mm)	Nb	C	Mn	Si	N
Nb-free steel	879	544	1.1	0.001	0.034	0.98	0.2	0.008
Nb-steel	897	567	1.1	0.084	0.031	0.83	0.2	0.006

Transmission electron microscopy (TEM) studies were carried out using a JEOL 2100 at 200 kV. Atom probe tomography (APT) work was performed using a Local Electrode Atom Probe (LEAP) at ~25 K with a pulse fraction of 25%, a flight path of 90 mm and a pulse repetition rate of 200 kHz. All TEM and APT specimens were prepared from the centre of the steel sheets in the thickness direction.

Results

The N pick-up measured after nitriding is shown in Table 2. N levels in the samples nitrided for 4 and 6 h were 7.4 and 9.3 times higher than the as-received sample.

The hardness profiles (Fig. 1a) showed significant hardening for the Nb-steel. Surface hardening to a lesser extent was also observed in nitrided Nb-free steel. Table 2 shows the tensile data from the nitrided steels. There was a small drop of total elongation from 14% to 12% after 4 h. The fracture type still remained ductile. The YS and UTS of the 4 h nitrided Nb-steel were 52% and 43% higher than those of the as-received steel. Further nitriding (6 h) caused a dramatic drop in ductility that lead to brittle fracture.

Table 2 N content, yield strength, ultimate tensile strength and elongation of Nb-steel with 525°C nitriding.

Nitriding time (h)	N (wt%)	YS (MPa)	UTS (MPa)	TE (%)
0	0.007	475.9±1.7	557.1±4.7	14.2±2.3
1	0.025	600.0±2.3	673.0±2.6	11.7±0.2
4	0.059	722.0±1.4	797.5±4.9	12.5±0.5
6	0.072	764	822	5

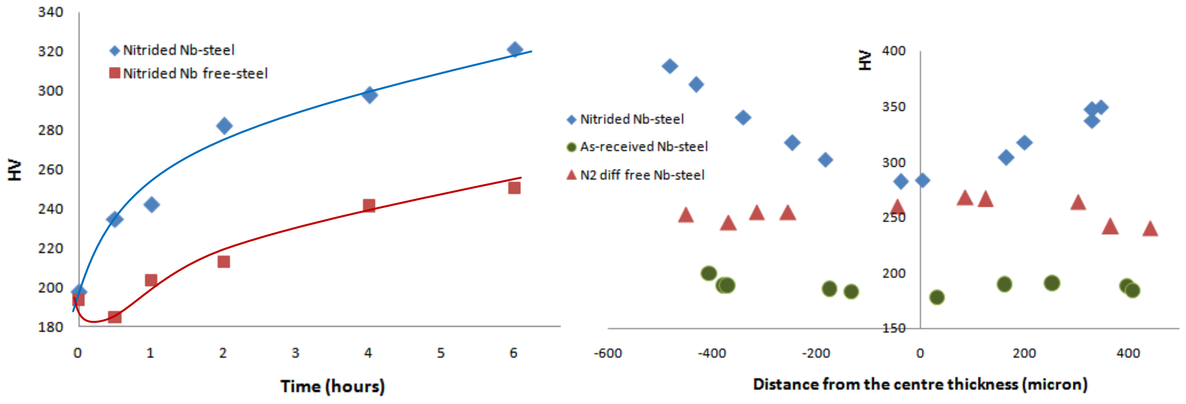

Figure 1 a) Hardness vs nitriding time, b) Hardness profiles through the thickness of the as-received, nitrided and N diffusion-free Nb-steels. The latter two specimens were aged for 4 h at 525°C.

The hardness profiles of the 4 h-nitrided Nb-steel, 4 h-heat-treated Nb-steel without N diffusion and the as-received Nb-steel in the thickness direction are plotted in Fig. 1b. The hardness of the as-received and the N diffusion-free were uniform across the thickness, but the heat-treated sample was harder. The nitrided Nb-steel was harder towards the surfaces and softer near the centre. The centre hardness values were only slightly higher than that of N-diffusion-free aged steel.

TEM observations revealed a very fine, speckled contrast after nitriding for 4 to 6 h, indicating a dispersion of very fine precipitates (Fig. 2a). The specimens nitrided for 6 h also contained coarse features along grain boundaries (Fig 2b). These features were occasionally found in the 4 h - nitrided steel but less frequently. Such features were not seen in the as-received steels.

Atom probe also showed a dispersion of fine precipitates in the specimens nitrided for 4 and 6 h (Fig. 2c). Precipitates were observed along dislocations as well as in the matrix. No Nb-rich precipitates were found in atom probe data from the as-received steel. There were also noticeable $(NbN)^{3+}$ and $(NbN)^{2+}$ clusters present in 4 and 6 h-nitrided Nb-steels.

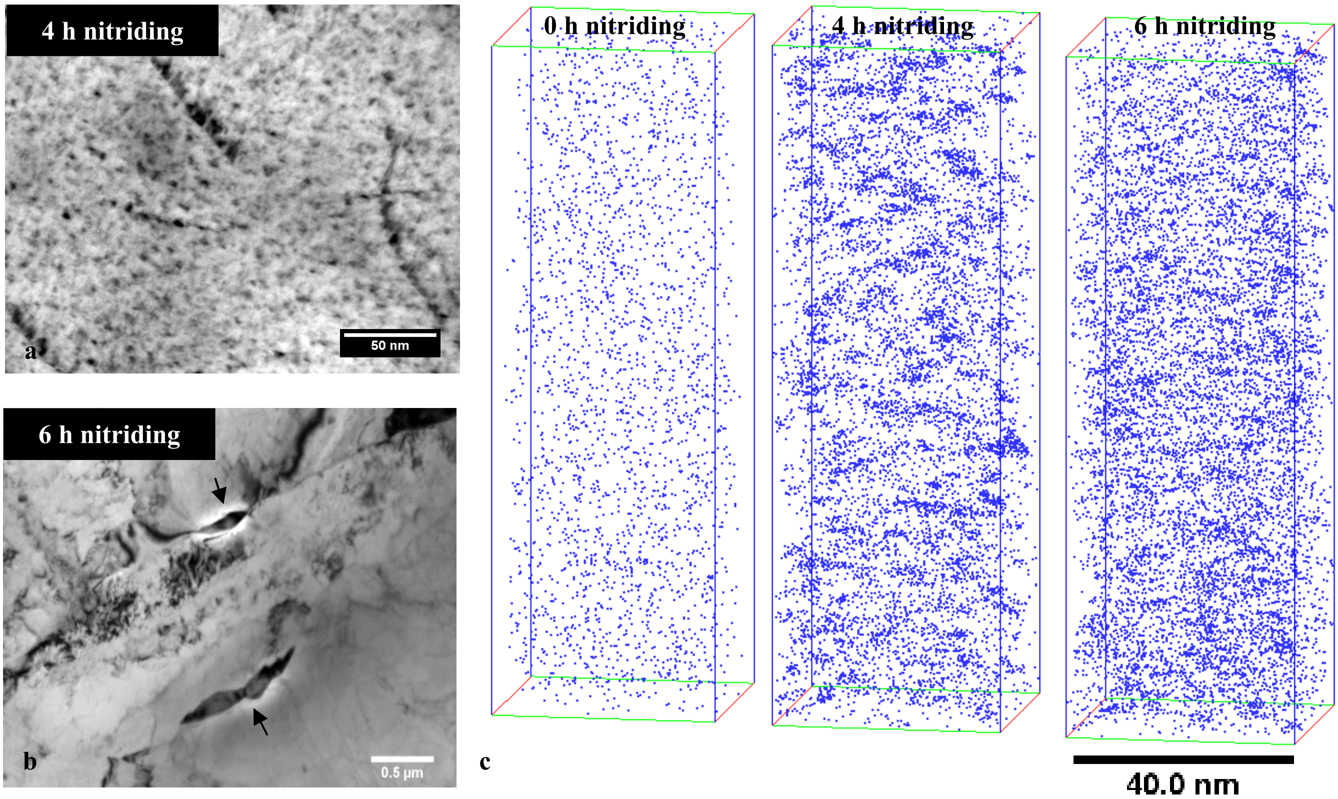

Figure 2 a) and b) TEM images showing a) precipitates in the Nb-steel nitrided for 4 h and b) coarse grain boundary precipitates in the Nb-steel nitrided for 6 h. c) APT data showing the distribution of $(NbN)^{3+}$ and $(NbN)^{2+}$ complex ions in the as-received, 4 h and 6 h-nitrided Nb-steels.

Discussion

Nitriding using KNO_3 salt bath resulted in a 50% increase in yield strength of the Nb-steel after 4 h, accompanied by only a small drop in total elongation from 14% to 12% compared to as-received steel. Fig. 1 shows that nitriding improves the surface hardness of the Nb-steel substantially, agreeing well with the tensile data. The surface hardness of the Nb-free steel was also strengthened by nitriding to a lesser extent. Strengthening/hardening of Nb-steel by nitriding is thought to result from combined solid solution strengthening [7] and dispersion strengthening by Nb-rich precipitates.

Due to the low initial N content (0.007 wt%) in the as-received steel, the N diffusion behavior can be approximated using the N diffusion in ferrite model [4-6]. Using the equations described in reference [8], the diffusion coefficient of N in ferrite (D_N^α) at 525°C is calculated to be 3.06×10^{-12} $m^2 s^{-1}$ [8,9]. The salt bath is assumed to be able to provide infinite amount of N during nitriding due to its large quantity, so the N concentration at depth x (C_x) can be calculated using the non-steady state diffusion model described in [4-6]. If the nitriding distance (x) is defined as the depth where $C_x = C_s / 10$, then the nitriding distance can be expressed as $x = 2.32\sqrt{D_N^{\alpha} t}$

The diffusion depth after 4 h nitriding is estimated to be 0.49 mm, which is about half the thickness (0.50 mm) of steel sheet with the scale removed. Therefore, after 4 h nitriding, the N concentration near the surfaces is higher than that near the centre and this is reflected by the hardness measurements in Fig. 2. Detailed characterization is difficult to achieve as TEM and APT results obtained from small volumes do not fully explain the overall mechanical properties. In order to ensure the consistency in this study, all TEM and APT specimens were made near the centre of the steel sheets

Hardening effects were also observed in the non-nitrided aged steel due to formation of Nb(C, N) precipitates [3]. As expected, no variation in hardness was observed in the through-thickness direction. The hardness of the centre of the nitrided Nb-steel was similar to the N diffusion-free aged Nb-steel, implying that only a small amount of N diffused into the centre region. This agrees well with the calculated value of the N diffusion distance (about half the steel sheet thickness). Therefore, good strength and ductility were achieved in the 4-h nitrided steel by combining hard surfaces with a more ductile core.

The diffusion depth after 6 h nitriding is estimated to be 0.57 mm, which is more than the half thickness (0.50 mm) of the steel sheet with scale removed. Coarse features along grain boundaries were consistently observed in TEM specimens prepared close to the centre of the steel sheets. Since the N solubility in ferrite at room temperature is very low (<0.0001 wt%) [7], a large fraction of the additional N segregates to grain boundaries forming coarse precipitates, most likely iron nitride.

Conclusions

This study investigated the strengthening mechanism of nitriding on a Nb-microalloyed steel compositions made by twin roll casting at 525° C in a KNO_3 salt bath. Nitrided Nb-steel exhibited higher surface hardness than nitrided Nb-free steel treated with the same conditions. Optimised mechanical properties were obtained after 4 h nitriding, with an approximate 50% increase in yield strength and only a small loss of ductility. TEM and APT observations suggest this results from a combined effect of interstitial solid solution strengthening and dispersion strengthening by fine Nb-rich precipitates. Cross-sectional hardness variations were consistent with calculated values of N diffusion. Coarse features along grain boundaries observed in 6-h nitrided steel are thought to be responsible for brittle fracture in these samples.

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