Effect of Thermal Cycle and Nitrogen Content on the Hot Ductility of Boron-bearing Steel

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Hot ductility of Boron (B)-bearing steel has been examined in view of slab corner cracking problem. Addition of B to the low carbon steel reduced its hot ductility under a thermal cycle in which samples were cooled directly to the test temperature before straining. The change in hot ductility of B-bearing steel with deformation temperature showed one trough in the temperature range of 800–1 000°C, which covered the lower temperature region of austenite single phase (region (I)), and near the austenite/ferrite transformation temperature (Ae3) (region (II)). An abrupt temperature decrease and reheating before straining heavily deteriorated the hot ductility of B-bearing steel in the region (I). In all steels, the strain concentration in the film-like ferrite primarily reduced hot ductility in region (II) regardless of the addition of B and the thermal cycles before straining. The ductility reduction of B-bearing steel is caused by the distribution and amount of BN precipitation, which is determined by the thermal cycles and the N content. Increase in the N content remarkably reduced hot ductility of B-bearing steel in region (II), where the behavior of BN precipitates controlled hot ductility. The results shows that the improvement of hot ductility in B-bearing steel can be attained by decreasing the N content and by avoiding an abrupt temperature decrease in the secondary cooling stage of the slab after solidification.

KEY WORDS: corner crack; hot ductility; Boron-bearing steel; BN precipitation; N content; thermal cycle.

1. Introduction

The problem of surface cracking of continuously cast steel slabs has been extensively investigated.1–3) These investigations have led to alloying and process modifications that have greatly reduced surface cracking, but difficulties are still encountered for micro-alloyed steels. The advent of thin slab casting with hot direct rolling (HDR) requires new techniques tailored to the conditions of this process. Because surface inspection before HDR is not possible, surface cracks must be eliminated from slabs if rolling products are to be defect-free. Therefore, defect-free slab surface is a prime requirement for the economic production of steel by HDR.4–6) One approach to making slabs that are free of surface cracks is to add alloying elements to improve the steel’s hot ductility.6–8)

Addition of B to plain carbon steel improves hot ductility in the austenite single-phase region because solute B atoms that segregate to grain boundaries can occupy vacancies and thus prevent formation and propagation of micro-cracks at grain boundaries.9,10) However, in B-bearing steel, transverse cracking on the slab surface easily occurs during continuous casting (CC) process because of poor hot ductility at temperatures of 700–1 000°C, possibly due to formation of Boron Nitride (BN) at austenite (γ) grain bound-
aries.11)

The diffusion coefficient of B in low carbon steel is on the order of 10^{-10} m^2/s at ~1 200°C.12) The diffusion coefficient of Nitrogen (N) in Fe at ~1 200°C is slightly less than that of B, and that of a metallic elements13) such as Cr in Fe at ~1 200°C is on the order of 10^{-13} m^2/s.14) These coefficients indicate that both B and N diffuse faster and can travel farther in steel than can metallic elements. Therefore, BN precipitates are thought to have a variety of distributions in the steel in by thermal or mechanical treatment. Also, controlling BN precipitation behavior by adjusting the N content, is thought to change the hot ductility of B-bearing steel.

Generally, temperature cycling occurs in the slab surface during secondary cooling of continuous casting, e.g., water spray on the surface causes a rapid temperature drop and recalescence causes the temperature to rise again. In the present study, the influences of thermal cycling and N contents on the hot ductility of B-bearing steels were investigated and a possible way of improving the hot ductility of CC slabs of the steels was suggested.

2. Experimental Procedure

Five types of steels were used in this study; they contain
almost the same concentration of elements except for B and N (Table 1). To quantify the effect of B addition on the hot ductility, 0.0015% or 0.0025% B were added to the plain carbon steel (C-steel). Also, steels with different N content were prepared to investigate the effect of N content on hot ductility of steel containing 0.0025% B. It is well known that the addition of Ti in B-bearing steels is a usual practice for preventing BN formation and increasing solute B content. However, in this study, Ti was not added to the B-bearing steel for the investigation of effect of N content on the B precipitation behavior in the various thermal cycles.

Steel ingots were casted by vacuum induction melting furnace then hot rolled into 20 mm thick plates with a final rolling temperature of 1 000°C. The tensile specimens were machined from each plate with their longitudinal axis parallel to the rolling direction; each such specimen had a diameter of 7 mm with a gauge length of 10 mm.

The equilibrium temperature of austenite/ferrite phase boundary (Ae₃) calculated using Thermo Calc (Thermo Calc software, Inc.) was about 876°C, which indicated that proeutectoid ferrite was not formed above 900°C in all steels. Therefore, the temperature above 900°C was designated here as the austenite (γ) region and below 850°C as the austenite/ferrite (γ+α) region. Hot tensile tests were conducted using a hot deformation simulator with dilatometer in an inert atmosphere of Argon gas. The reduction of area (RA) was measured to evaluate hot ductility.

Two kinds of thermal cycles were used to evaluate hot ductility of steels (Fig. 1). Cycle (A) corresponds to a thermal cycle for conventional measurement of hot ductility. Cycle (B) simulates the practical CC process, in which the slab is rapidly cooled and then reheated after it is existed from the mould. In the secondary cooling part in CC process, the temperature of the corner of the slab may decrease to the lower temperature region of γ or to the γ+α region; the cycle (B) represents schematically these thermal cycles.

The fractured specimens were examined, both metallographically and fractographically, by optical microscopy, scanning electron microscopy, and transmission electron microscopy (TEM). Also, some samples were directly quenched by water spraying to preserve the pro-eutectoid ferrite and the B precipitates that formed at the test temperature. Carbon extraction replicas taken from cross-sections prepared in the vicinity of fracture surfaces were examined by TEM and TEM-energy-dispersive X-ray Spectrometry (TEM-EDS). B distribution within specimens was determined using Particle Tracking Autoradiography (PTA) analysis. The B-detecting sensitivity of this method is 0.0001% and the spatial resolution is 2 μm.

3. Results

3.1. Hot Ductility of B-bearing Steel in the Thermal Cycle (A)

Figure 2 showed hot ductility curves for the investigated steels in the thermal cycles (A), in which specimens cooled to the test temperature from solution treatment temperature of 1 350°C with the cooling rate of 20°C/s. The hot ductility of the C steel (B free) is decreased by addition of B particularly in the lower temperature region of γ (900–1 000°C). However, the change of B contents from 0.0016 to 0.0024% had little influence on deterioration of the hot ductility of C–B steel (B bearing).

Figure 3 showed that the effect of N content on the hot ductility of C–B steels (0.0025% B) in the thermal cycles (A). The increase of N content from 0.0011 to 0.0049% decreased hot ductility of C–B steels in the lower temperature region of γ, and this trend was similar to that caused by addition of B (Fig. 2).

However, in the α+γ region (<850°C), the results of the hot ductility measurement in Fig. 2 and Fig. 3 indicated that the variation of B and N contents had little influence on the hot ductility. Figure 4(a) shows typical longitudinal cross sectional micrographs of C steel, and the micrographs were...
similar for all the tested steels. Film-like ferrite formed along γ grain boundaries at 850°C. The fracture mode in this temperature was shallow dimple fracture, although it was macroscopically inter-granular, as shown in Fig. 5. In the lower temperature region of γ single phase (900–1000°C), hot ductility of C–B steels (0.0025% B) decreased, it exhibited dependence on N content; the increased in N content deteriorated hot ductility as well (Fig. 3). It is clear from these results that the change of N content affects the behavior of B precipitation in the lower temperature region of the γ single phase.

For the C–B steel (0.0025% B) of higher N content
samples deformed in the temperature range of 900–950°C, no ferrite was observed as expected from the \( A_{\text{e}3} \) temperature, the cracks were typical ones produced by grain boundary sliding (Fig. 6). The inter-granular fracture was observed in the samples fractured in this temperature region \( (\gamma \text{ region}) \) giving very poor ductility, as shown in Fig. 7(a). The fracture surfaces were generally much flatter (Fig. 7(b)).

Fig. 7. Fracture surface of C–B steel \((0.0024\% \text{ B, } 0.0049\% \text{ N})\) in thermal cycle \( (A) \) quenched after fracture at 900°C \((a) \times 20, (b) \times 200.\)

Fig. 8. Bright field image, EDS spectrum, X-ray maps of a precipitate in C–B steel \((0.0024\% \text{ B, } 0.0049\% \text{ N})\) at 900°C \( (a) \) Bright field image, \( (b) \) EDS spectrum of the precipitates, \( (c) \) X-ray map of precipitate.

Fig. 9. Ion micrographs showing the distribution of B and N in C–B steel \((0.0025\% \text{ B, } 0.0049\% \text{ N})\) at 850°C \( (a) \) \( {^{11}}\text{B}^{+} \) ion micrograph, \( (b) \) \( {^{14}}\text{N}^{+} \) ion micrograph.

\((0.0049\% \text{ N})\) samples deformed in the temperature range of 900–950°C, no ferrite was observed as expected from the \( A_{\text{e}3} \) temperature, the cracks were typical ones produced by \( \gamma \) grain boundary sliding (Fig. 6). The inter-granular fracture was observed in the samples fractured in this temperature region \( (\gamma \text{ region}) \) giving very poor ductility, as shown in Fig. 7(a). The fracture surfaces were generally much flatter (Fig. 7(b)).
To identify the precipitates, TEM observation of the fracture surface was performed by the carbon extraction method. Figure 8 represents precipitates on the fracture surfaces; these precipitates were identified as BN by TEM-EDS and X-ray mapping (Figs. 8(a) and 8(c)). SIMS analysis was also conducted to identify the composition of precipitates, as shown in Fig. 9. The secondary $^{11}$B/^{10}$ ions and the secondary $^{14}$N/^{10}$ ions didn’t present a linear form in the grain boundaries; instead, they coagulated into granule along grain boundaries or within the matrix. Also, the secondary $^{11}$B/^{10}$ ion distribution corresponds to that of secondary $^{14}$N/^{10}$ ions in the B-steel. These results indicate that B and N atoms in the C–B steels exist as precipitates, and not as segregated solutes.

For the C–B steel (0.0025% B) of lower N content (0.0011% N), ductility was excellent in the temperature range of 900–950°C as dynamic recrystallization had occurred, and no grain boundary precipitation of BN and γ grain refinement was observed when this steel quenched from 900°C after fracture (Fig. 10(a)). Fractures at this temperature only occurred with pronounced necking, and the fracture surface was the dimpled rupture type (Fig. 10(b)).

To account for the differences in the hot ductility between high- and low-N content steels, PTA examinations were performed to identify the BN distribution in the C–B steel before deformation. Figure 11 shows BN distribution of the C–B steel with different N contents in the temperature range of 900–1000°C. When the N content was low (0.0011% N), a relatively few BN precipitates occurred; these were sparsely distributed in the matrix. However, when the N content was high (0.0049% N), a relatively large number of BN precipitates occurred; these are densely distributed in the interior of the grain as well as the grain boundary. Moreover, increase in N content also increased the temperature at which BN could precipitate.

### 3.2. Hot Ductility of B-bearing Steel in the Thermal Cycle (B)

Hot ductility curves of C–B steel (0.0025% B) for the...
thermal cycle (B), where the temperature was once dropped to 600°C or 900°C (under-cooled temperature) and then heated up to the straining temperature (>900°C), together with that for the thermal cycle (A) are shown in Fig. 12, respectively. A comparison of the thermal cycle (A) and cycle (B) shows that there is a widening of the trough to a temperature of ~1000°C in the latter case. At the temperature range of 900–1100°C, low hot ductility in thermal cycle (B) was associated with the BN precipitation behavior was similar to those found at the temperature range of 900–950°C in the thermal cycle (A).

Figure 13 showed BN distribution in the C–B steel before deformation with the different under-cooled temperatures and reheating temperatures. Large numbers of BN precipitates were observed in prior γ grain interiors and prior γ grain boundaries when the under-cooled temperature was 600°C (Fig. 13(a)). Moreover, large numbers of preferential BN precipitates on the γ grain interior and boundary also occurred when the under-cooled temperature was 900°C (Fig. 13(d)). These precipitates of BN remained undissolved in γ when the reheating temperature was 1000°C, as shown in Figs. 13(b) and 13(e). The results from Figs. 13(c) and 13(f) indicate that the BN precipitates re-dissolve into austenite when the reheating temperature was 1200°C.

The effects of the N contents on the hot ductility of C–B steel (0.0025% B) in the thermal cycle (B) were shown in Fig. 14. From this result, the decrease in N content led to improvement of hot ductility at reheating temperature range of 900 to 1200°C at both under-cooled temperatures. Figure 15 showed the effects of the thermal cycles and the N content on the hot ductility of C–B steel (0.0025% B) at a fixed straining temperature of 1100°C. The tensile testing temperature of 1100°C was chosen, because very high ductility of C–B steel was obtained at this temperature in thermal cycle (A) even when the N content was high (0.0049% N). The C–B steel containing low N content (0.0011% N) exhibited very high ductility in the under-cooled temperature range of 600–1000°C, but those with higher N content show decreased hot ductility as the under-cooled temperature decreased.
4. Discussion

4.1. Causes of Hot Ductility Loss in B-bearing Steel in the Temperature Range 800 to 1000°C

Hot ductility of the B-free steel (C steel) decreased at 850°C, the temperature at which proeutectoid ferrite forms at the austenite grain boundary (Fig. 4(a)). Hot ductility loss in this case is caused by non-uniform deformation between the γ and α phase due to their strength difference at the temperature. However, the ductility in the steel increased in the single γ temperature range from 1000 to 900°C (region I), because this temperature range is high enough for dynamic recrystallization to be sufficiently developed to isolate grain boundary cracks, preventing them from joining up (Fig. 4(b)).

Adding a small amount of B to the C steel decreased hot ductility in region (I); hot ductility trough expanded to the region (I) (Fig. 2). Generally, the hot ductility of micro-alloyed steel is sensitive to the effect of austenite grain size (AGS) and the precipitation at γ grain boundaries in region (I). Hot ductility of the steel increases as the AGS decreases. Also, precipitations at the γ grain boundary cause decrease in the hot ductility by grain boundary sliding and preventing the grain boundary movement. In the present instance the C and C–B steels all had almost the same AGS (~500 μm) in region (I), i.e. the effect of adding B on the AGS had a little effect on the hot ductility. Therefore, formation of BN at the γ grain boundary seems to be responsible for the hot ductility loss of C–B steel in the region (I).

4.2. Effect of N Content on Hot Ductility of B-bearing Steel

In the C–B steel (0.0025% B), increasing the N content from 0.0011 to 0.0049% decreased the hot ductility in the region (I) (Fig. 3). For the C–B steel with high N content (0.0049% N), hot ductility loss in region (I) is due to the large number of BN precipitates in the interior of the prior γ as well as preferentially at the γ grain boundaries (Figs. 11 (h) and 11(i)). Especially, BN precipitates which have a smaller inter-particle spacing at the γ grain boundaries are more effective at pinning these boundaries; it cause cracks formed by grain boundary sliding (Fig. 6). The grain boundary sliding in the γ grain boundary leads to occurrence of inter-granular fracture with flatter surface (Fig. 7). In contrast, hot ductility of C–B steel with low N content (0.0011% N) in region (I) is excellent due to a relatively small number of BN precipitates (Figs. 11(a) and 11(b)), because the small number of precipitates causes an absence of grain boundary pinning, which in turn results in formation of dynamic recrystallization by isolating grain boundaries from developing cracks (Fig. 10 (a)). These results demonstrate that a difference of BN distribution due to the change of N content is likely to correlate with the volume fraction of BN precipitates in the temperature range at which they start to precipitate out.

The results from Fig. 14 to Fig. 15 indicate that the effect of N content on the hot ductility of the C–B steel in the thermal cycle (B). Decrease in the N content led to formation of a relatively smaller number of BN precipitates in the matrix during both under-cooled temperatures of 600°C and 900°C before straining. This reduction in the quantity of BN precipitates improves the hot ductility of C–B steel. These results are explained that increase of N content in the C–B steel give rise to increase of volume fraction of BN precipitation and to promotion of BN precipitation in the higher single γ temperature region. Therefore, the larger volume fraction of BN precipitation caused by increasing the N content in the C–B steel causes BN precipitates to occur at the grain boundary in region (I), which enhances grain boundary sliding and increases the temperature at which dynamic recrystallization occurs.

Yamamoto et al., in their study on B-Ti-bearing steels, found that if the N content satisfied the condition; (wt%N–0.2×wt%Ti)<0.003 wt%, there was no embrittlement by BN occurring at γ grain boundaries. As shown in Fig. 3 and Fig. 14, the decrease of N content, in our B-bearing steel, give rise to the improve of hot ductility. These results indicate that reduction of N content is beneficial to solve corner cracking problems in the B-bearing steel.

4.3. Effect of Temperature Cycle before Straining on Hot Ductility of B-bearing Steel

To investigate the effect of temperature cycle before straining on the hot ductility, thermal cycle (B) was applied to the hot tensile test. Generally, the hot ductility at constant straining temperature and strain rate is influenced by variation of the precipitation behavior caused by the temperature cycle before straining. In thermal cycle (A), the steel was directly cooled to the straining temperature range of 1000 to 1100°C; this direct cooling leads to formation of small amount of BN precipitates (Fig. 11(g)), and increases the hot ductility of C–B steel. In contrast, in thermal cycle (B), a large number of the BN precipitates formed at the under-cooled temperatures of 600°C or 900°C (Figs. 13(a) and 13(d)) remain as undissolved precipitates at the straining temperature range of 1000–1100°C (Figs. 13(b) and 13(e)). These undissolved precipitates decrease the hot ductility of C–B steel at this temperature. However, an increase in the straining temperature (>1200°C) led to dissolution of a large fraction of BN precipitates in γ (Figs. 13(c) and 13(f)); the resulting decrease in the amount of BN precipitates at this temperature improves the hot ductility of C–B steel. These results indicate that the change of hot ductility in the C–B steel corresponds with the precipitation and dissolution behavior of BN in response to the temperature cycles before straining.

4.4. The Preventing of Corner Cracking in the B-bearing Steel

One of the most important results of the present investigation is that the hot ductility loss in the B-bearing steel occurs in the temperature range at which BN precipitates at γ grain boundaries. In order to avoid the surface cracks on the B-bearing steel slab, Yamamoto et al. also propose that cooling rate keeps less than 0.5°C/s in the secondary cooling zone to promote precipitation of coarse BN. However, it seems sometimes difficult to realize the slow cooling rate in actual slab casting process. Especially in the slab corner, thermal cycle usually occurs during secondary cooling zone of slab caster. In this work, it has been shown that there is an effect of thermal cycles on hot ductility of B-bearing
steel. As shown in Fig. 12, hot ductility of B-bearing steel is decreased by a large under-cooling and reheating in hot tensile test. From an industrial point of view, to reduce the incidence of corner cracking in B-bearing steel slabs, the amplitudes of the under-cooling and the reheating cycle in the unbending zone of CC strand should be as small as possible.

5. Conclusion

Hot ductility of B-bearing steel was investigated by hot tensile tests under two types of thermal cycles (direct cooled to straining temperatures, under-cooled and reheated to straining temperatures). The effect of N content on the hot ductility of B-bearing steel was also investigated. The following conclusions were obtained.

(1) Addition of B to plain Carbon steel deteriorated hot ductility under the thermal cycle which introduced direct fast cooling to straining temperature because of the precipitation of BN in the lower temperature region of the γ single phase.

(2) The rapid temperature drop and reheating to straining temperature heavily deteriorated hot ductility of the B-bearing steels because the precipitation of BN was encouraged. The thermal cycle before straining leads to formation of a large number of BN precipitates in the B-bearing steel.

(3) PTA results showed that the hot ductility of B-bearing steel depended strongly on the distribution of BN precipitates, which were in turn determined by thermal cycle and N content of the steels. With high N content; BN precipitates were randomly distributed in the interior of the prior austenite and preferentially at austenite grain boundaries. Whereas, the precipitates were rather sparsely distributed and larger in the B-bearing steel of low N content.

(4) High hot ductility in the B-bearing steel can be obtained by the avoiding a fast temperature drop below 1000°C in the secondary cooling stage of the slab after solidification, and the amplitudes of the under-cooling and the reheating of the thermal cycle in CC strand should be small.

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