CONTROL OF NITROGEN CONTENT FOR THE IMPROVEMENT OF HAZ TOUGHNESS IN Ti-CONTAINING STEEL

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ABSTRACT

The variation of HAZ toughness with nitrogen content and weld cooling rate was investigated and interpreted in terms of both microstructure and the amount of free nitrogen. The presence of free nitrogen in HAZ was investigated by internal friction measurement and its amount was measured by hydrogen hot extraction analysis. Both nitrogen content and weld cooling rate influenced HAZ microstructure and high toughness was obtained at a mixed microstructure of acicular ferrite, ferrite sideplate and polygonal ferrite. If nitrogen content is too low or cooling rate is too fast, bainitic microstructure is obtained and toughness is low. On the other hand, if nitrogen content is too high or cooling rate is too slow, coarse polygonal ferritic microstructure is obtained and toughness is deteriorated again. In addition to the microstructural change, high nitrogen content also resulted in a large amount of free nitrogen. Therefore, nitrogen content should be kept as low as possible even if the mixed micostructure is obtained. In this experimental condition, the maximum toughness was obtained at 0.006% nitrogen content when weld cooling time ($\Delta t_{8/5}$) is 60s.

KEYWORDS

HAZ toughness, TiN particles, microstructure, free nitrogen, hydrogen hot extraction analysis

1. Introduction

Intensive studies have shown that the addition of titanium to steel is one of the most effective methods of improving its heat-affected zone (HAZ) toughness. It has been demonstrated that fine TiN particles prevent the coarsening of austenite grains in HAZ and also act as heterogeneous nucleation sites for the ferrite transformation during a weld cooling cycle, thereby resulting in fine microstructure [1-2]. To obtain a homogeneous and fine TiN particles distribution, the contents of titanium and nitrogen and manufacturing process should be controlled adequately. Kasamatsu *et al* investigated [3] the effect of titanium and nitrogen contents on the size and distribution of TiN particles and showed that the number of the particles increases with an increase of nitrogen content. Watanabe *et al* reported [4] that a substantial amount of TiN precipitated when the nitrogen content of steel was increased above 0.004% and there was a strict control of the rolling process. In general, steel with high nitrogen content is considered as having an unsatisfactory weldability due to 'free' nitrogen, which impairs toughness in the HAZ. Cuddy *et al* showed [5] that steels containing titanium and nitrogen in excess of 0.02 and 0.007% respectively had poor HAZ toughness independent of microstructure. Thus, even in Ti-containing steels, they suggested that nitrogen levels must be kept low. However, some other results are contradictory. Zajac *et al* showed [6] that high nitrogen steel (0.013% N) has higher HAZ toughness than low nitrogen steel (0.003% N) if microalloying elements such as titanium and vanadium are carefully balanced in the composition and the welding parameters are selected adequately. They showed that the excess nitrogen, that is, not combined as TiN, enhanced TiN stability and resulted in small austenite grain in HAZ. The amount of nitrogen in solid solution is further reduced by reprecipitation of vanadium nitrides during the weld cooling cycle. From all these previous results it is clear that the effect of nitrogen on HAZ toughness of Ti-containing steel is very complicated depending on the nitrogen content, welding parameters and microalloying elements etc.

In this paper is examined the effect of nitrogen content over a wide range (0.0006~0.016%) on the simulated HAZ toughness of Ti-containing steel that was manufactured by the thermomechanically controlled-rolled process (TMCP). The variation of HAZ toughness with nitrogen content and weld cooling rate was investigated and interpreted in terms of both microstructure and amount of free nitrogen. The presence of free nitrogen in HAZ was confirmed by internal friction measurement and its amount was measured by hydrogen hot extraction analysis.

2. Materials and Experimental Procedures

Seven 0.14% C-1.5% Mn steels were melted using a vacuum induction furnace with almost constant Ti content, 0.02%, and various N contents, 0.0006~0.016%. After soaking the ingot at 900°C for one hour, it was thermomechanically controlled-rolled to the final thickness of 12.5mm. Final analyses and mechanical properties of the plates are presented in Table 1. In addition to titanium, approximately 0.0010% of boron was also added in Steels E and F. Precipitate particles in base plates and simulated HAZs were observed using carbon extraction

Table 1 Chemical composition and mechanical properties of steels used

	Chemical composition (wt. %)							Mechanical properties				
	C	Si	Mn	Al	Ti	B	N	TS (Mpa)	YS (Mpa)	El (%)	H_V (1kg)	$_VE_{-20}$ (J)
A	0.13	0.11	1.53	0.04	0.02	-	0.0006	641	372	13	177	337
B	0.14	0.11	1.58	0.04	0.02	-	0.006	594	460	13	180	205
C	0.14	0.10	1.51	0.05	0.02	-	0.011	576	493	13	179	176
D	0.14	0.11	1.53	0.05	0.02	-	0.013	573	461	14	183	203
E	0.15	0.10	1.56	0.04	0.02	-	0.016	591	509	12	195	227
F	0.14	0.11	1.54	0.05	0.02	0.0013	0.006	589	407	12	181	128
G	0.15	0.10	1.52	0.05	0.02	0.0010	0.010	600	413	11	185	105

replicas by a scanning transmission electron microscope (STEM) operating 200kV. Specimens for HAZ simulation were subject to the weld thermal cycle using a weld thermal cycle simulator. The applied thermal cycle is defined by a 135°C/s heating rate, 1350°C peak temperatures (T_P), a 5s holding time at the peak temperature and a 10~150s cooling time from 800°C to 500°C ($\Delta t_{8/5}$). After the thermal cycle, standard 2mm V-notch Charpy impact test specimens were machined and tested at -20°C.

Internal friction measurement and hydrogen hot extraction analysis were carried out to determine the amount of free nitrogen in HAZ. The specimen for internal friction measurement was obtained from the HAZ near the fusion boundary of CO_2 welded plate in the form of sheet, 1x5x110mm. Internal friction was measured using a torsion pendulum apparatus (Sinkuriko IFM 1500-M) in the temperature range –30~240°C with pendulum frequency 2.3Hz. For the hydrogen hot extraction analysis, 2g of needle shape millings is placed in a combustion boat and introduced into a tube furnace at temperature 450°C with an argon flow of 0.3*l*/min. Gas flow is then switched to hydrogen at 0.3*l*/min. After four hour, the gas flow is changed back to argon and the sample is cooled downed in the furnace. Nitrogen content of the samples before and after exposure to the hydrogen atmosphere was measured by the LECO inert gas fusion process. The free nitrogen value is given by the difference between them.

3. Results and Discussion

To study the effect of nitrogen content on the precipitation of TiN particles, particle size distribution in the base plate and HAZ ($\Delta t_{8/5}$ 60s) of Steel B (0.006% N) and E (0.016% N) were observed using carbon extraction replicas. The number of particles in the size range of less than 5nm up to 100 nm was counted at 5nm class interval within an area of approximate 8.4μm^2. Little difference was observed in the base plate. The mean particle size and number density of Steel B and E are 7.2, 8.4nm and 2.1x10^8, 1.7x10^8/mm^2, respectively. However, difference was shown in the HAZ with 16.8, 10.3nm and 0.3x10^8, 1.1x10^8/mm^2, respectively. TiN particles were coarsened in the HAZ of both steels. However, the degree of coarsening is different and Steel E has more fine particles than Steel B. According to Zener equation, as more effective inhibition of grain growth is obtained with larger volume fraction of fine particles, Steel E is expected to have smaller austenite grain size than Steel B in the HAZ. Indeed this effect was observed in other experiments. Zajac *et al* showed [6] that the austenite grain size is about three times larger in low nitrogen steel (0.003% N) than in high nitrogen steel (0.013% N), despite the manufacturing process and level of Ti and V. Continuous cooling transformation (CCT) diagrams of both steels were constructed and compared to study the effect of nitrogen content on the phase transformation in HAZ. After austenitizing at 1350°C for 5s, the hollow cylindrical shape specimens were cooled with various cooling rates to obtain dilatation curves. Figure 1 shows CCT diagrams of both steels. The

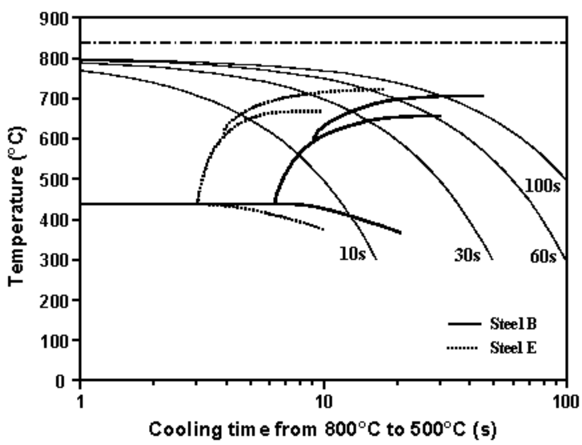

Fig. 1 Comparison of SH-CCT diagrams of Steels B and E

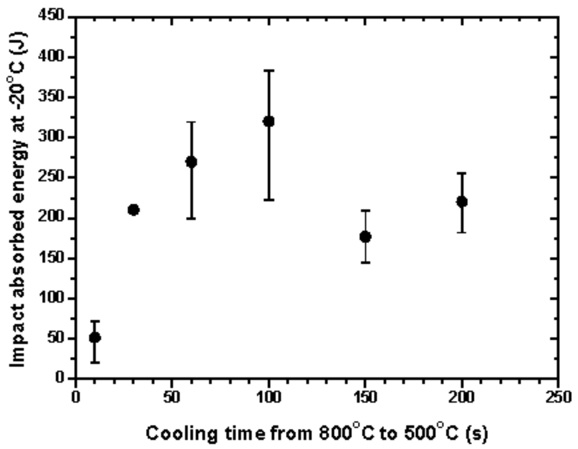

Fig. 2 Variation of HAZ impact absorbed energy as a function of cooling time from 800°C to 500°C (Steel B)

diagram of high nitrogen steel (Steel E) is shifted to shorter time periods to accelerate phase transformation in HAZ. This low hardenablity of Steel E is believed due to the smaller austenite grain size. The low coarsening rate of TiN particles in the high nitrogen steel can be readily explained using Wager equation. Under condition of diffusion control, the rate of change of particle radius is directly related to the concentration of the rate limiting specie. In the case of TiN particles, the relevant solutes are titanium and nitrogen, for which the diffusion coefficient of titanium is many orders of magnitude lower than that of nitrogen, and results in titanium being the rate-limiting specie. Using solubility product of TiN, the soluble titanium content in HAZ with peak temperature 1350°C was estimated. It is about 0.0005% for Steel E and 0.0041% for Steel B, showing lower concentration of soluble titanium in Steel E. Therefore, increase of nitrogen content results in smaller austenite grain size due to the low coarsening rate of TiN and thus accelerates phase transformation in HAZ.

To study the relationship between HAZ microstructure and toughness, a variety of HAZ microstructure were produced by changing cooling time ($\Delta t_{8/5}$). Figure 2 shows the variation of HAZ impact absorbed energy of Steel B with $\Delta t_{8/5}$. It increases gradually with an increase of cooling time and shows maximum value 320J at 100s and then decreases again with further increase of cooling time. Optical microstructure observation showed only upper bainitic microstructure at 10s. Meanwhile, it was comprised of acicular ferrite, ferrite sideplate and fine polygonal grainboundary ferrite at 60 and 100s, and mostly coarse polygonal ferrite at 150 and 200s. This result suggests that instead of upper bainite or coarse polygonal ferrite a mixed microstructure of acicular ferrite, ferrite sideplate and fine polygonal ferrite should be obtained to have high HAZ toughness. Figure 3 shows the variation of HAZ impact absorbed energy with nitrogen content when $\Delta t_{8/5}$ is constant as 60s. After showing low value, 48J, at 0.0006% N (Steel A), it increases up to 270J (Steel B) at 0.006% N (Steel B) and then decreases again and shows only 25J at 0.016% N (steel E). Optical microstructure observation showed that Steel A has upper bainitic microstructure even though $\Delta t_{8/5}$ is relatively long as 60s. All other steels have a mixed microstructure of acicular ferrite, ferrite sideplate and polygonal ferrite. However, the volume fraction of polygonal ferrite in the mixed microstructure increases with an increases of nitrogen content and Steel E with the highest nitrogen content (0.016%) showed about 61% of polygonal ferrite and pearlite This microstructural change supports the observation of the effect of nitrogen on the acceleration of ferrite transformation in HAZ shown in Fig. 1. As Steel A has low nitrogen content (0.0006%), it shows bainitic microstructure due to the large austenite grain size and thus have low HAZ toughness. Improvement of HAZ toughness in Steel B is attributed to the formation of a mixed microstructure instead of bainite. However, even though other steels, especially Steels C and D, have the same mixed microstructure, their HAZ toughness are very low. This means that nitrogen content should be kept as low as possible even in the tough microstructure.

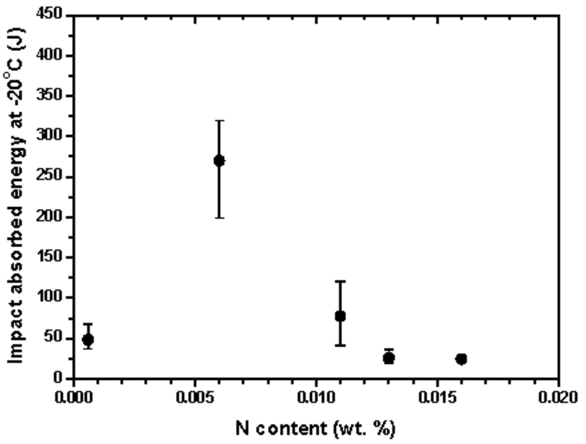

Fig. 3 Variation of HAZ impact absorbed energy as a function of nitrogen content ($\Delta t_{8/5}$, 60s)

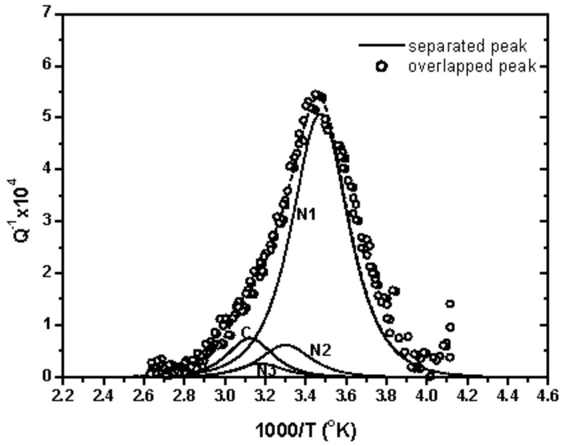

Fig. 4 Separation of measured internal friction curve of HAZ (Steel E)

Besides the effect of nitrogen on the HAZ microstructure mention above, the effect of free nitrogen present in HAZ should also be considered when optimizing nitrogen content in Ti-containing steel. Free nitrogen in HAZ can be present either by addition of nitrogen in excess of that required for stoichiometric combination with the titanium or by the dissolution of nitrides during weld thermal cycle. In this study, the presence of free nitrogen in the HAZ was confirmed first by internal friction measurement. As alloy elements such as silicon and manganese give rise to extra Snoek peaks in addition to normal peaks in pure α-iron, it is difficult to interpret the internal friction curve obtained in carbon-manganese steels. den Ouden investigated [7] an internal friction of ferritic CO_2 weld metal and showed that the influence of manganese is most significant. In addition to the two normal Snoek peaks at 22.5 and 39.5°C with activation energies of about 18,600 and 20,100 cal/mol, respectively, the presence of manganese gives to four extra peaks at 7°, 34°, 82° and 132°C at a pendulum frequency of 1.05Hz with activation energies of about 16,000, 19,500, 20,000 and 21,000 cal/mol, respectively. He also calculated the internal friction, Q^{-1}, of each peak with the assumption that the observed internal friction at temperature T can be considered as being the sum of the contributions of the different peaks. Following him, internal friction was measured using specimens obtained from HAZ of Steel E and the observed internal friction curve was separated into each peaks. It was separated into four different peaks as shown in Fig. 4. N2 and C peaks with internal friction of 0.62×10^{-4} and 0.75×10^{-4}, respectively, are normal peaks, and N1 and N3 peaks with internal friction of 5.08×10^{-4} and 0.26×10^{-4}, respectively, are extra peaks due to the presence of manganese. It is clear that free nitrogen under influence of manganese atom is present in the HAZ of Steel E.

Using hydrogen hot extraction analysis free nitrogen content in the HAZ of each steel was measured quantitatively. After applying weld thermal cycle of $\Delta t_{8/5}$ 60s, samples were prepared and analyzed following the procedure mentioned before. Figure 5 shows the variation of free nitrogen content with the nitrogen content of steel. It increases gradually with an increase of nitrogen content and Steel E with the highest nitrogen content (0.016%) shows about 0.005%, which is about 30% of the nitrogen content added. From this result, it can be seen that low HAZ toughness of Steels C, D and E with a mixed microstructure is related to the large amount of free nitrogen. To interpret the effect of free nitrogen on HAZ toughness, HAZs with same microstructure should be considered because HAZ toughness is also influenced by the microstructure. Figure 6 compares the impact absorbed energy of Steels B, C and D, which have the same mixed microstructure. As Steels A and E have bainite and relatively a large amount of polygonal ferrite, respectively, they are excluded in the comparison. It decreases linearly with an increase of free nitrogen and Steel B with 0.0009% free nitrogen has 270J while Steel D with 0.0034% has only 25J. The slope of the line in the figure indicates that the HAZ impact absorbed energy with the mixed microstructure decreases by about 97J per 0.001% free nitrogen. Figure 4 also shows the free nitrogen content of Steels F and G which have about 0.001% boron. Being compared at the same nitrogen level, the steels have lower free nitrogen content, 0.0004% in Steel F and 0.001% in Steel G, than other steels. The beneficial effect of boron on the reduction of free nitrogen was reported in several other experiments. It was observed that free nitrogen present at high temperature was fixed by boron to form boron nitrides due to the high diffusivity of boron. Even though the addition of boron is effective on the reduction of free nitrogen, its amount should be controlled carefully because boron also tend to segregate on the austenite grain boundaries and increases hardenability to change microstructure as well.

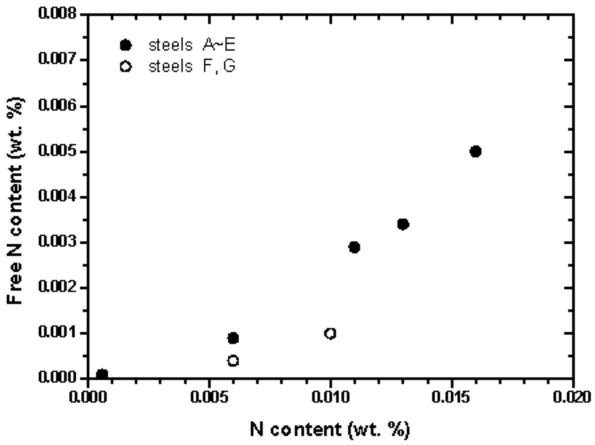

Fig. 5 Variation of HAZ free nitrogen content as a function of nitrogen content in base plate

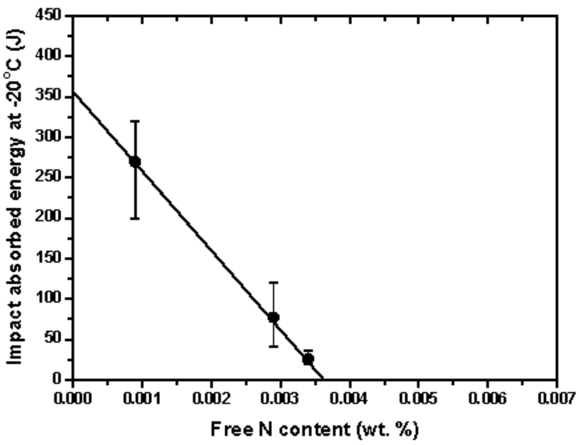

Fig. 6 Comparison of HAZ impact absorbed energy as a function of free nitrogen content of Steels B, C and D

4. Conclusions

Both weld cooling rate and nitrogen content should be controlled to have high HAZ toughness of Ti-containing steel. As cooling rate decreases, HAZ microstructure changes from bainite to a mixed microstructure of acicular ferrite, ferrite sideplate and polygonal ferrite and toughness improves. However, if it is too low, microstructure becomes coarse polygonal ferrite and toughness deteriorates again. With an increase of nitrogen, microstructure changes from bainite to the mixed microstructure due to the effect of acceleration of ferrite transformation and thus toughness improves. However, an increase of nitrogen content also increases the amount of free nitrogen, it should be kept as low as possible even if the mixed microstructure is obtained. In this experimental condition, maximum toughness was obtained at 0.006% nitrogen content when weld cooling time ($\Delta t_{8/5}$) is 60s

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