Micromechanism of local brittle zone phenomenon in weld heat-affected zones of advanced 9% Ni steel

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9% Ni steel has been widely used around the world as a material for the inner walls of liquefied natural gas (LNG) storage tanks because of its excellent cryogenic fracture toughness at or below 111 K, the boiling temperature of LNG. A new quenching, larmellarizing and tempering (QLT)-processed 9% Ni steel was developed and recently has been used as a material for super-sized LNG tanks because it enhances cryogenic toughness considerably over the conventionally heat treated 9% Ni steels such as quenching and tempering (QT) and double normalizing and tempering (NNT)-processed ones [1].

Like other structural steels, the QLT-9% Ni steels experience welding processes during the construction of the tanks. It is now widely recognized that a small zone of abnormally low fracture toughness, referred to as a local brittle zone (LBZ), can exist in the heat-affected zones (HAZs) of multi-pass welded structural steel. In general, the coarse-grained HAZ (CGHAZ) adjacent to the fusion line has the lowest toughness among various regions within HAZ because of unfavorable microstructure such as large prior austenite grain size [2–4]. Metallographic analyses reveal that CGHAZ can be roughly categorized into four characteristic zones according to the peak temperature of subsequent thermal cycle in a multi-pass welding procedure: (i) unaltered CGHAZ (UA CGHAZ), the region reheated above specific temperature of grain growth or not reheated at all, (ii) supercritically reheated CGHAZ (SCR CGHAZ), the region reheated above A_{C3}, (iii) inter-critically reheated CGHAZ (IC CGHAZ), the region reheated between A_{C1} and A_{C3}, and (iv) sub-critically reheated CGHAZ (SC CGHAZ), the region reheated below A_{C1}. Many studies have been conducted on the LBZ phenomena observed in these CGHAZs for the various structural steels, used mainly for offshore structures [2–4]. However, for cryogenic steel such as 9% Ni steel, there have been few studies on the existence and behavior of LBZs at cryogenic temperature, and far fewer researches are available for QLT-9% Ni steel HAZ. The present work was undertaken to clarify the LBZ phenomenon of QLT-treated 9% Ni steel using simulated HAZ specimens.

The 9% Ni steel used in this study is a commercial grade for LNG storage tanks in Korea, whose chemical composition is 0.066C-0.24Si-0.65Mn-0.005P-0.005S-9.28Ni. The steel plates are normally processed by the QLT (Q; 1093 K for 60 min, quench, L; 963 K for 80 min, quench, and T; 853 K for 60 min, quench) heat treatment.

For weld simulations, oversized Charpy specimen blanks ($11 \times 11 \times 60$ mm) were thermally cycled in metal thermal cycle simulator (MTCS). After reaching the first peak temperature (T_{P1}) concerning CGHAZ of 1623 K, the specimens were cooled down with the constant cooling time from 1073 K to 773 K ($\Delta t_{8/5}$) of 13.5 and 19.4 s. The cooling rates were approximately equivalent to those of a submerged arc welding (SAW) and shielded metal arc welding (SMAW) processes with heat inputs of 23 kJ/cm and 28 kJ/cm, respectively, in a 22-mm-thick plate [5]. These simulated welding conditions were based on the actual welding conditions for the tanks in Korea [1]. The peak temperature of the second weld thermal cycle (T_{P2}) was varied between 1473 K and 823 K. The Charpy V-notch impact specimens were machined from the simulated specimen blanks and then tested at 77 K.

The results of the Charpy impact tests at 77 K are shown in Fig. 1, as a function of the peak temperature of the second thermal cycle. In the figure, the second thermal cycles with peak temperatures between 1473 K and 1373 K simulate UA CGHAZ while the cycles between
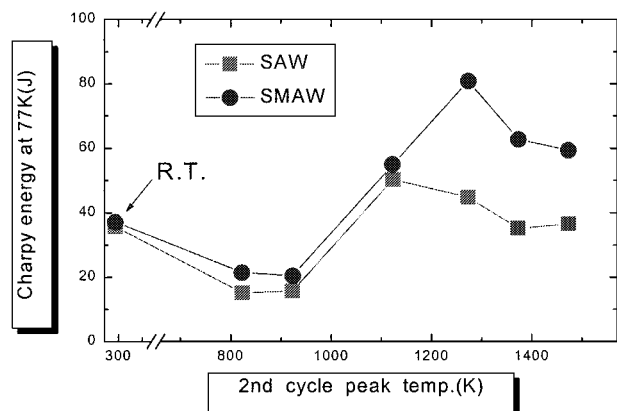

Figure 1 Relation between Charpy impact energy at 77 K and the second peak temperature.

1273 K and 1073 K simulate SCR CGHAZ, and the cycles between 923 K and 823 K simulate IC CGHAZ, respectively. SC CGHAZ was not considered in this study because the properties of the SC CGHAZ were expected to be similar or superior to those of the UA CGHAZ due to its low peak temperature and tempering effects. The both results of SMAW and SAW exhibit the lowest Charpy impact energies in the case of IC CGHAZ, and the values are lower than the minimum impact value of improved 9% Ni steel at 77 K, 35 J, as required in the various standards such as BS 7777 [6]. So, it is possible to correlate that the IC CGHAZ is the primary LBZ of QLT-9% Ni steel. Otherwise, the specimens simulating the SCR CGHAZs show the highest values.

To find the micromechanism controlling the cryogenic LBZ phenomenon of the IC CGHAZ, microstructural analyses were performed. First, the microstructures of the simulated CGHAZs were observed by optical microscopy. As shown in Fig. 2, the UA and IC CGHAZs consist of coarsened microstructure of prior austenite grains and martensite laths. On the other hand, the SCR CGHAZs have fine grains because the second thermal cycle above A_{C3} changed the coarse grained microstructure to the fine-grained microstructure through recrystallization. Although the change in grain size may be correlated to the highest toughness of the SCR CGHAZs among the CGHAZs, the grain size variation alone cannot account for the dif-
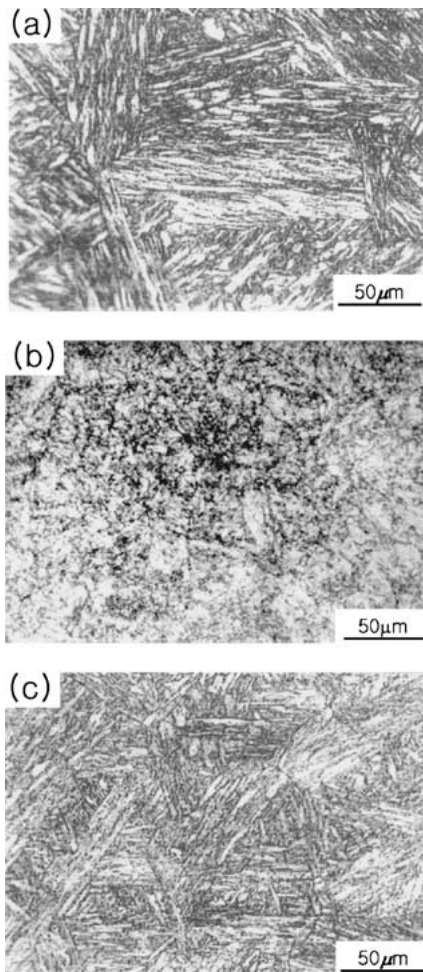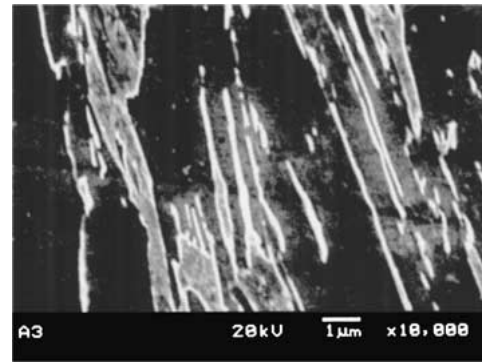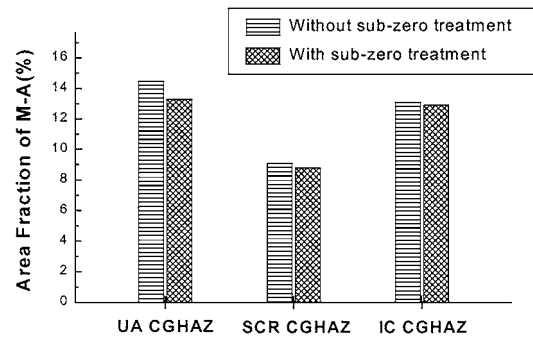

(a)

(b)

Figure 3 Results of M-A constituents observations; (a) an example of scanning electron micrographs of the M-A constituents, and (b) change in the M-A fraction within the simulated CGHAZs.

Figure 2 Optical micrographs of the (a) simulated UA CGHAZ, (b) simulated SCR CGHAZ, and (c) simulated IC CGHAZ.

ference in toughness between UA CGHAZs and IC CGHAZs.

The martensite-austenite (M-A) constituent, a microstructure with high carbon contents and thus high hardness value, is generally known as one of the main factors that reduce the toughness in the HAZs of high strength structural steel [2–4]. Therefore, the M-A constituents of the simulated CGHAZ specimens were observed by scanning electron microscopy (SEM) and the area fraction of the M-A constituents was measured by image analyzer using the specimens with and without sub-zero treatment at 77 K. For the SEM observation of the M-A constituents, the specimens were etched by two stages electrolytic etching technique [2]. Fig. 3 shows an example of the observed M-A constituents and the change in the M-A area fraction within the simulated CGHAZs. The difference in the M-A fractions between the sub-zero treated and untreated specimens is very small. Comparing the change in the M-A fraction with the Charpy energy variation, it is evident that the LBZ phenomenon of the IC CGHAZs at cryogenic temperature could not be explained by the change in M-A area fraction alone. This result is of a great interest, since until now the amount of the M-A constituents has been treated as the most important factor in the LBZ phenomenon of the IC CGHAZ in many studies on high strength structural steel HAZs [2–4].

The authors also estimated the carbon content in the M-A constituents of each CGHAZ specimen quantitatively using electron probe X-ray micro-analyzer (EPMA). The carbon content is generally known as an effective indicator on the hardness of the martensite phase. Fig. 4 shows the representative examples of
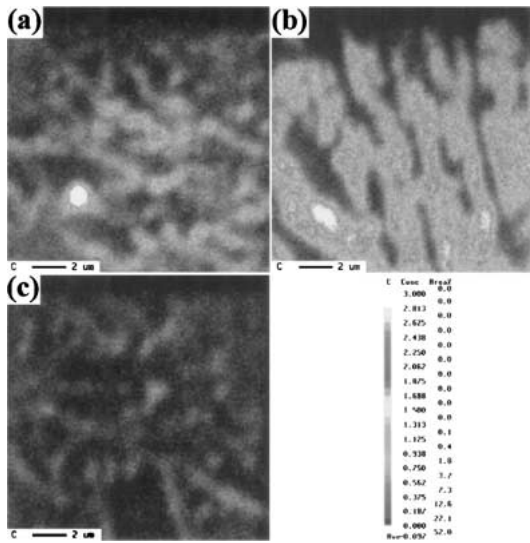
Figure 4 Results of EPMA estimation of the carbon contents in the M-A constituents of simulated CGHAZ; (a) simulated SCR CGHAZ, (b) simulated IC CGHAZ, and (c) simulated UA CGHAZ.

EPMA results. The results of EPMA exhibit that the average values of the carbon contents are 0.75%, 1.1%, and 2.2% in the case of UA, SCR, and IC CGHAZ respectively.

The carbon content variation could be explained by the difference in the peak temperature during the second thermal cycle, as schematically illustrated in Fig. 5. On reheating a CGHAZ above A_{C1}, austenite nucleated and grew preferentially along the prior austenite grain boundaries and martensitic lath boundaries. However, since there was insufficient time for the diffusion of substitutional elements, mainly Ni, the austenite became enriched only in the interstitial element, i.e., carbon [4]. When the peak temperature of the second thermal cycle (T_{P2}) is between A_{C1} and A_{C3}, as in the case of IC CGHAZs, carbon concentration of the islands (C_1 in Fig. 5) is much higher than that of the matrix (C_0 in Fig. 5). When T_{P2} is above A_{C3}, as in the case of SCR CGHAZs, austenite islands would form at high carbon areas such as prior austenite grain boundaries from which carbon atoms would diffuse out but could not because the temperature is not high enough to provide
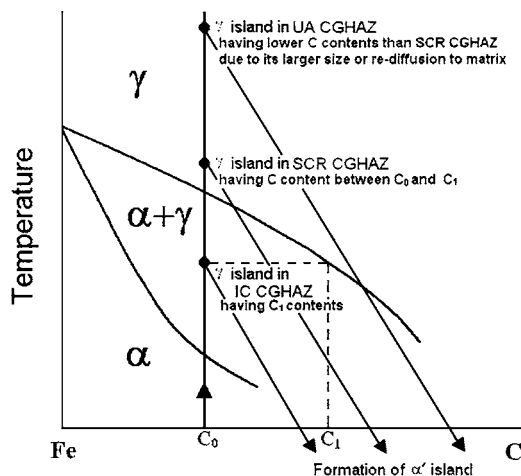

Figure 5 Schematic diagram to explain a mechanism for the variation of carbon content in the M-A constituents in the CGHAZs during the reheating cycle sequence.

the necessary mobility. Thus, carbon concentration in the austenite islands would be at a level between C_0 and C_1. When T_{P2} is above the grain growth temperature, as in the case of UA CGHAZs, austenite islands would grow, and at the same time, martensitic microstructures of matrix will also transform to austenite. So, the rediffusion of carbon from austenite islands to matrix would make the average carbon content in the islands of UA CGHAZs smaller than those of SCR CGHAZs. During the cooling sequence, the carbon-enriched austenite islands have to transform mostly to martensite islands, i.e., M-A constituents, and the carbon concentration of the islands increases. The increase is due to the fact that the carbon in martensite matrix diffuses to neighboring islands, which results from insufficient time for long-range diffusion. In the present work, the carbon content of about 2.2 wt% in the case of IC CGHAZ is very high compared to the carbon content of the base metal, about 0.06 wt%. However, the carbon content of 2.2 wt% is within the range of the previous works that showed the carbon contents in the M-A constituents could be up to 2.6 wt% [7, 8], or at least consistent with the assertion that there is no relationship between carbon contents in the base material and those in the M-A constituents [9].

Based upon all the results obtained, the LBZ phenomenon of the IC CGHAZs in this study could be explained by the following mechanism. Hrivnak *et al.* [10] suggested the empirical relationship for the M-A constituents between their Vickers hardness (H_{M-A}) and carbon content (C wt%) as Equation 1.

$$C(\text{wt}\%) = \frac{H_{M-A} - 15}{575} \qquad (1)$$

Although the exact value of hardness cannot be obtained from the above equation, the relative change in hardness among the CGHAZs can be evaluated. In the cases of UA CGHAZs and SCR CGHAZs, the calculated hardness values of the M-A constituents are 447 H_v and 648 H_v, respectively. However, in the case of IC CGHAZs, it is about 1280 H_v. Since the average Vickers hardness of the HAZs in the QLT-9% Ni steel is about 400 H_v as found in a previous work [1], it can be recognized that the IC CGHAZs have the largest strength mismatch between the M-A constituents and neighboring matrix among the CGHAZs while UA CGHAZ have little mismatch between them.

Chen *et al.* [11] proposed that the stress concentration and triaxiality of the neighboring matrix increase by the hard phase particles such as the M-A constituents and the stress in the neighboring matrix can be raised up to several times of the average stress. In the light of their suggestion, the matrix surrounding M-A constituents in the IC CGHAZ of this steel will be plastically constrained more than in other CGHAZs. At cryogenic temperature, the plastic deformation of the matrix is not easy and then not able to relieve the high stress concentration and triaxiality. So, brittle cracking will occur and propagate. In the case of UA CGHAZs, although the M-A fraction is a little larger than that in the IC CGHAZs, a significant increase in the stress does not exist in the matrix because the carbon

content in the M-A constituents is very low. Therefore, the main factor affecting toughness decrease in the UA CGHAZs at cryogenic temperature is not the existence of M-A constituents, but mainly the coarse grain size. In the case of SCR CGHAZs, although the M-A constituents in the SCR CGHAZ are harder than those in the UA CGHAZs due to the high carbon contents in M-A, the fine grain size and the relatively small volume fraction of the M-A constituents result in the higher toughness.

It could be concluded that, unlike in other studies on the various structural steels [2–4], the LBZ phenomenon of the IC CGHAZs in this steel cannot be explained simply by the change in M-A fractions, but is mainly associated with relatively high carbon contents in M-A of the IC CGHAZs.

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