The Effects of Grain Boundary Phosphorus Segregation and Heat Treatment on Toughness of 9 % Ni Steel and Its Welded Joint

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Effects of phosphorus (P) and heat treatment on toughness have been investigated on a quenched and tempered 9 % Ni steel base metal and its welded joint simulated by a thermal cycle simulator. The mechanism of toughness improvement by the diminution of P component was examined by mechanical tests, microstructure observation and computer simulation of the grain boundary segregation. The critical CTOD value and Charpy absorbed energy in the base metal showed remarkable deterioration as increasing P content, when the cooling rate after tempering was lower than 1×10^{-2} K/s. Simulated bonds showed reduction of toughness when the P level was higher than 0.008 % and/or the cooling rate after post weld heat treatment (PWHT) was lower than 1×10^{-2} K/s. The Charpy absorbed energy of base metal was higher than that of PWHT welded joint when they showed the same critical CTOD value. Intergranular ductile fracture was occurred in the base metal, while intergranular brittle fracture in PWHT welded joint was observed.

The effect of cooling rate following the tempering on the grain boundary segregation of P was estimated by computer simulation, based on Guttman-McLean theory. The computed amount of P segregation in grain boundary was closely related to the toughness both for a base metal and a simulated bond. It was also suggested that when the grain boundary segregation of P was lower than 0.1, high toughness level was obtained in the base metal and the simulated bond. The difference of toughness between the base metal and the simulated bond was attributed to the coarsening of grain size by the welding thermal cycle. The 9 % Ni steel with P level lower than 0.005 % shows excellent toughness in the base metal and the welded joint.

KEY WORDS: 9 % Ni steel; LNG storage tank; fracture toughness; phosphorus; welded joint; computer simulation.

1. Introduction

With recent advances in steelmaking technology, impurities, such as P and S in steel have been reduced to extremely low level.¹⁾ In 9 % Ni steel for large LNG storage tanks, very high toughness level is required to achieve very severe safety criterion. It is known that S reduces ductility of 9 % Ni steel, however brittle fracture property is not severely dependent on S level.²⁾ While the diminution of P is one of the prominent ways to improve toughness in 9 % Ni steel.

The production of 9 % Ni steels with low P level has been realized in the manufacturing process.³⁾ However, the mechanism of toughness improvement by the diminution of P has not been cleared. For the purpose of determinating the optimum P level to improve the toughness of 9 % Ni steel, the effect of P segregation must be investigated. One of the obvious detrimental effects of P on toughness is temper embrittlement, as shown in an extensive study in Cr-Mo steel.⁴⁾ The interaction between Ni and P has an important role on properties of 9 % Ni steel, but its mechanism has not been clear.

The purpose of the present study is to examine the effect of P on toughness in both a base metal and a welded joint of 9 % Ni steel. The mechanism of the embrittlement, related P, was investigated by scanning electron microscope and Auger electron spectroscopy.

Computer simulation was carried out to study the effect of P level and thermal cycle on the grain boundary segregation of P.

2. Experimental Procedure

2.1. Materials

9 % Ni steels with P level ranging from 0.001 to 0.013 % were examined. Chemical composition of the steels is shown in Table 1. These materials were prepared by vacuum melting and cast into the moulds with 150 mm thickness. Then they were hot rolled to slabs of 110 mm thickness. The slabs were austenized at 1 523 K for 60 min, rolled to a final thickness of 20 mm at temperature range from 1 373 to 1 223 K. Total reduction by 5 passes was 83 %. The plates were heated at 1 053 K for 70 min, water quenched and then tempered at 843 K for 80 min. In order to examine the effect of cooling rate after tempering on toughness, specimens were cooled by three kinds of cooling rate; water cooling (40 K/s), air cooling (5×10^{-1} K/s) and furnace cooling (1×10^{-2} K/s). Fig. 1 schematically shows the manufacturing process.

In order to simulate the bond of shielded metal arc welding (SMAW) with heat input of 4.6×10^3 J/mm for 16 mm plate, thermal cycle was applied to the air cooled specimens by induction heating and

Table 1. Chemical composition of 9 % Ni steels tested.
(wt%)

Steel	C	Si	Mn	P	S	Ni
1	0.053	0.26	0.62	0.001	0.0009	9.32
2	0.052	0.24	0.67	0.005	0.0009	9.13
3	0.056	0.26	0.62	0.008	0.0009	9.12
4	0.061	0.26	0.62	0.013	0.0008	9.14

Fig. 1. Manufacturing process of 9 % Ni steel.

Fig. 2. Thermal cycle simulating shielded metal arc welding.

cooling device. The employed thermal cycle is shown in Fig. 2.

The specimens after the thermal cycle treatment were heated at 833 K for 120 min, and then cooled with cooling rates of 1×10^{-2} and 6×10^{-2} K/s in order to investigate the effect of post weld heat treatment (PWHT) on toughness in 9 % Ni steel. It should be noted that the minimum cooling rate used for normal PWHT conditions corresponds to 6×10^{-2} K/s.

2.2. Experimental Method

The effect of P on toughness was examined by Charpy impact test and crack opening displacement (CTOD) test in accordance with British Standard BS 5762.⁵⁾ 10 mm thickness specimens with transverse crack propagation direction were machined from the plate, in which both upper and bottom surfaces of the plate were eliminated.

Fractured surface was examined by scanning electron microscope (SEM) with an accelerating voltage of 100 kV. Grain boundary segregation of P was

examined by scanning micro Auger electron spectroscopy (AES) with beam diameter of 500 Å. The change in P with sputtering time was also investigated.

2.3. Computer Simulation of Grain Boundary Segregation of P

Accurate quantitative evaluation of the grain boundary segregation in 9 % Ni steel is very difficult because of the impossibility of brittle fracture of specimens inside micro Auger equipment at low temperature such as 108 K. So, grain boundary segregations of the base metal and the simulated bond were estimated by computer simulation using a model based on Guttman-McLean theory.⁶⁾

Equilibrium concentration of P on grain boundary, $X_P(\infty)$, is given by the following equation:

$$X_P(\infty) = \frac{X_P^B \exp(\Delta G_P^B/RT)}{1 + X_P^B[\exp(\Delta G_P^B/RT) - 1]}, \quad \dots\dots\dots(1)$$

where, R : gas constant

T : temperature

X_P^B : bulk atom fraction of P

and ΔG_P^B is segregation energy of P described as follows⁷⁾:

$$\Delta G_P^B = 10.5 + \alpha_{NiP} \cdot X_{Ni} \text{ (kcal/mol)}, \quad \dots\dots\dots(2)$$

where, α_{NiP} : interaction parameter between P and Ni

X_{Ni} : bulk atom fraction of Ni.

The value of α_{NiP} in the present simulation was 6.2 kcal/mol.⁷⁾

The time, required for the grain boundary to reach its equilibrium concentration, depends on diffusion rate of segregation element through alloys. A solution of the diffusion equation corresponds to segregation to a planer interface for dilute alloys takes form⁸⁾:

$$\frac{X_P(t) - X_P(0)}{X_P(\infty) - X_P(0)} = 1 - \exp\left(-\frac{4Dt}{\alpha^2 d^2}\right) \operatorname{erfc}\left[\left(\frac{4Dt}{\alpha^2 d^2}\right)^{1/2}\right], \quad \dots\dots\dots(3)$$

where, D : diffusivity of P through steel

d : the thickness of the segregated interface region (assumed to be one mono layer)

$X_P(t)$, $X_P(0)$: grain boundary atom fractions of P at times t and 0, respectively

α : the ratio of equilibrium grain boundary atom fraction of P, $X_P(\infty)$, to bulk atom fraction, X_P^B .

The diffusivity D is given by⁹⁾:

$$D = 1.58 \times 10^4 \cdot \exp(-52300/RT) \text{ (m}^2/\text{s)} \quad \dots\dots\dots(4)$$

With use of Eq. (3), P concentration on grain boundary during heat treatment is simulated.

3. Results

3.1. Effects of P Level and Heat Treatment on Toughness of 9 % Ni Steel

Fig. 3 shows the effect of P on Charpy absorbed

Fig. 3. Effect of P content on the Charpy absorbed energy at 77 K in quenched and tempered 9 % Ni steel, where cooling rates after tempering were 40, 5×10^{-1} and 1×10^{-2} K/s.

energy at 77 K in the quenched and tempered 9 % Ni steel. The effect of P level on absorbed energy is strongly related to the cooling rate after tempering. When the cooling rate is high, the test material containing 0.013 % P shows good impact properties. In the cooling rate of 1×10^{-2} K/s, the Charpy absorbed energy of specimens with P level higher than 0.008 % decreases markedly.

The CTOD test result is shown for cooling rate of 1×10^{-2} K/s in Fig. 4. The critical CTOD value, δ_c , decreases with increase of P level. This result is consistent in that of Charpy test.

Fig. 5 shows the relation between P content and Charpy absorbed energy of specimens after the thermal cycle simulating SMAW and PWHT. The P level dependence on the absorbed energy at 108 K is very small in the materials of as received condition. However, in PWHT the energy decreases with the increase of P. The effect of cooling rate on toughness after PWHT is also shown. The deterioration of absorbed energy by PWHT is observed in steel even if P content is 0.001 % for the cooling rate after PWHT is 1×10^{-2} K/s. However, when the cooling rate after PWHT is 6×10^{-2} K/s, the decrease of absorbed energy is small below 0.005 % of P content and service temperature of 108 K is shown to be within the upper shelf energy region. Consequently, the welded joint of 9 % Ni steel with ultra low P content shows excellent toughness both in as welded condition and PWHT with the cooling rate of 6×10^{-2} K/s.

Relations between δ_c and P level in specimens of as welded condition and PWHT with cooling rate of 1×10^{-2} K/s are shown in Fig. 6. The effect of P on δ_c of as welded condition is small, which is consistent in the Charpy impact test result. The decrease of δ_c in specimen after PWHT is remarkable except for ultra low P level less than 0.005 %. When P level is as low as 0.005 % the decrease of δ_c is not observed even if the cooling rate is as slow as 1×10^{-2} K/s.

Fig. 4. Effect of P content on the critical CTOD value at 108 K in quenched and tempered 9 % Ni steel; the cooling rate after tempering was 1×10^{-2} K/s.

Fig. 5. Effect of P content on the Charpy absorbed energy at 108 K in simulated bonds of 9 % Ni steel.

Fig. 6. Effect of P content on the critical CTOD value at 108 K in simulated bonds of 9 % Ni steel.

3.2. Fractured Surface of Base Metal and Simulated Bond of 9 % Ni Steel

Fig. 7 shows scanning electron micrographs of fractured surfaces of the base metal and the simulated bond by Charpy tests. In the simulated bond after PWHT with the cooling rate of 1×10^{-2} K/s, intergranular brittle fractured surface area increases with increasing P level. In the base metal, however intergranular ductile fractured surface area increases with

(a), (d): $P=0.001\%$; (b), (e): $P=0.008\%$
(c), (f): $P=0.013\%$

Fig. 7. Scanning electron micrographs of fractured Charpy specimens of quenched and tempered steels ((a)–(c)) and simulated bonds which were subjected to PWHT ((d)–(f)), where cooling rate was 1×10^{-2} K/s for tempering and PWHT.

increasing P level. Similar results were obtained in fractured surfaces of CTOD test specimens.

Fig. 8 shows a scanning electron micrograph of fractured surface of the quenched and tempered 0.013%P–9%Ni steel after tempering with the cooling rate of 1×10^{-2} K/s. Identification of precipitates on the surface was performed by X-ray energy dispersive analyser in SEM. This indicates that the precipitate is a kind of phosphide.

3.3. Grain Boundary P Segregation

Fig. 9 shows surface condensations of P, C, and O on intergranular fractured surface of the simulated bond of 0.013% P level subjected to PWHT. These values were calculated by the peak rate of those to Fe (703 eV) revealed by micro Auger analysis. It was impossible to fracture the specimen inside the micro Auger equipment at low temperature. Therefore, specimens were fractured outside the equipment prior to analysis at 108 K. Because of possible contamination prior to the analysis, accurate quantitative analysis of segregation was difficult in these tests. However, the surface condensations of P, C, and O showed rapid decrease with sputter time as shown in Fig. 9. Therefore, intergranular segregation of P was clearly ob-

Fig. 8. Scanning electron micrograph of Charpy specimen of 0.013%P–9%Ni steel and X-ray dispersive analysis of precipitates.

Fig. 9. Surface condensations of P, C and O revealed by micro Auger analysis in simulated bonds of 9% Ni steel subjected to PWHT.

served, and it was more obvious on lower cooling rate.

The effect of P composition on grain boundary segregation of P was calculated by Eq. (3). The result is shown in Fig. 10. This figure also shows the effects

Fig. 10. Effect of cooling rate on grain boundary segregation of P estimated by computer simulation.

Fig. 11. Comparison of computed grain boundary segregation of P in simulated bond with that in base metal.

of the tempering cooling rate. Experimental data of the P segregation on grain boundary in materials with 0.013 % P, were also plotted in the figure.

The relation between P concentration on grain boundary and P content is shown for the simulated bond after PWHT and the base metal in Fig. 11. The difference between them was small, but, in both the materials, P segregation was relatively smaller in 6×10^{-2} K/s than in 1×10^{-2} K/s.

4. Discussion

4.1. Mechanism of Embrittlement Caused by P Segregation

In the case of slow cooling rate, Charpy absorbed energy and δ_c deteriorate with increase of P in both the 9 % Ni steel base metal after the quenched and tempered treatment and the simulated bond after PWHT. This phenomenon known as temper embrittlement is often observed in Cr-Mo steel.⁴⁾ It is considered that temper embrittlement results from intergranular fracture due to grain boundary segregation of P. Heat treatment conditions were evaluated by tempering parameter T_P ¹⁰⁾ as shown in Eq. (5).

$$T_P = (20 + \log t) \cdot T \cdot 10^3, \quad \dots\dots\dots(5)$$

where, t : holding time (h)

T : temperature (K).

The calculated T_P are 16.97×10^6 and 16.91×10^6 for tempering at 843 K for 80 min and for PWHT at 833 K for 120 min, respectively. No significant difference was obtained. Consequently, heat treatment conditions for tempering of base metal and PWHT of simulated bond are considered to be equal.

Fig. 12 shows relation between the δ_c and the Charpy absorbed energy at 108 K in the quenched and tempered 9 % Ni steels and the simulated bonds. The latter materials are subjected to PWHT. The relation between δ_c and absorbed energy in the simulated bond is different from that in the base metal. The absorbed energy in the base metal is higher than that in the PWHT simulated bond, when they show the same δ_c value. As shown in Fig. 7, intergranular ductile fracture was observed in the base metal, while intergranular brittle fracture was observed in the simulated bond after PWHT. Therefore, the difference of δ_c -Charpy absorbed energy relation is considered to result from the difference of fracture type.

Fig. 13 shows the effect of P on δ_c . The effect of P level on δ_c is similar in both the base metal and the PWHT simulated bond. The crack initiation properties of brittle fracture is still considerably influenced by P level.

Especially, in the case of slow cooling rate after the tempering of base metal or PWHT of simulated bond of 9 % Ni steel, P decreases the crack initiation energy in intergranular fracture. In the case of the base metal with relatively fine grain size, intergranular ductile fracture occurs in crack propagation stage. On the other hand, in the simulated bond, intergranular brittle fracture occurs in coarse grain structure. Therefore, the difference of fracture toughness between both materials are due to the difference of fracture process caused by P level and grain size effect.

4.2. Relation between Grain Boundary Segregation and Toughness

The Charpy absorbed energy decreases linearly with increasing grain boundary segregation. Relation between the computed P concentration on grain boundary and the Charpy absorbed energy is shown for the base metal after tempering at 77 K in Fig. 14. This figure suggests that the deterioration of impact properties in the base metal is attributed to the grain boundary segregation of P. This conclusion is also supported by the result of δ_c and computed P segregation on grain boundary.

Fig. 15 shows the effect of P grain boundary segregation computed by Eq. (3) on δ_c . The δ_c simply decreases with decreasing P concentration of grain boundary in both the base metal and the simulated bond. However the difference of δ_c between them is not due to the grain boundary segregation of P, because the computed grain boundary P segregation after the PWHT simulated bond is nearly equal to that of the base metal. Therefore, the deterioration

Fig. 12. Relation between the critical CTOD value and the Charpy absorbed energy at 108 K in quenched and tempered 9 % Ni steels and simulated bonds which were subjected to PWHT.

Fig. 13. Effect of P content on the critical CTOD value of base metals and simulated bonds of quenched and tempered 9 % Ni steel.

of toughness in the simulated bond is attributed to the coarsening of grain size by welding.

4.3. Application of the Computer Simulation for Controlling P and Heat Treatment

As shown in previous sections, the effect of P composition and thermal cycle on concentration of P on grain boundary can be estimated by the computer simulation. Charpy absorbed energy and δ_c of the base plate were closely related to computed P concentration on the grain boundary. If the P concentration on grain boundary is less than 0.1, high toughness level in 9 % Ni steel is obtained as shown in Figs. 14 and 15. With use of the computer simulation, the P level and heat treatment condition to satisfy the above condition can be determined. In the case of the P level lower than 0.005 %, the P grain boundary concentration does not exceed 0.1 for the cooling rate of as low as 2×10^{-2} K/s, which is lower than the minimum cooling rate of 6×10^{-2} K/s used for normal PWHT condition.

In the present simulation, the thermal cycle is divided into infinitesimal time steps and the finite difference equation derived from Guttman-McLean equation (3) is utilized. By which, P concentration

Fig. 14. Relation between computed grain boundary segregation of P and Charpy absorbed energy in quenched and tempered 9 % Ni steel.

Fig. 15. Effect of computed grain boundary segregation on δ_c of base metal and simulated bond.

was computed at each steps for the purpose of applying to complex heat cycles. If the interaction parameter between impurity and metal and diffusivity of impurity in steel are properly determined, the present simulation method can be applicable to various alloy steels.

The accurate quantitative analysis of concentration of impurities such as P on grain boundary is sometimes difficult, because breaking the specimen inside the AES is not easy. In such cases, the computer simulation becomes a useful tool to understand the acceptable impurity level and the required heat treatment to provide a good toughness value.

5. Conclusion

Effects of P on toughness were examined in the base metal and the welded joint simulated by thermal cycle of quenched and tempered 9 % Ni steel for LNG storage tanks. Mechanism of toughness improvement

by the diminution of P in steel was also investigated.

(1) Critical CTOD values and Charpy absorbed energy deteriorate accompanying intergranular ductile fracture in base metal with P level higher than 0.008 %, when a cooling rate after tempering is as low as 1×10^{-2} K/s.

(2) Critical CTOD values and Charpy absorbed energy deteriorate by intergranular brittle fracture in simulated bonds subjected by post weld heat treatment (PWHT) with the cooling rate of 1×10^{-2} K/s, when P level exceeds 0.008 %.

(3) Although similar CTOD values were obtained in both materials, the Charpy absorbed energy of the base metal is higher than that of PWHT simulated bond. Intergranular ductile fracture was observed in a base metal, while a PWHT simulated bond showed intergranular brittle fracture. The transition of ductile to brittle fracture mode is attributed to the coarsening of grain size by welding thermal cycle.

(4) Crack initiation properties of 9 % Ni of base metal and welded joint are influenced by P level. The critical CTOD value decreases with the increase of P level.

(5) By using computer simulation based on Guttman-McLean theory, the effect of cooling rate after tempering of steel on the grain boundary segregation of P in the base metal was estimated for the base metal. The computed grain boundary segregation of P is closely related to toughness of the base metal. The Charpy absorbed energy of the base metal decreases with the computed grain boundary segregation.

(6) The toughness of PWHT simulated bond is also dependent on the computed grain boundary seg-

regation of P. The difference of toughness between the base metal and the simulated bond is attributed to the coarsening of grain size by the welding thermal cycle.

(7) Computer simulation suggests that when the grain boundary segregation of P is less than 0.1, high toughness level is obtained in both the base metal and the welded joint. When P is lower than 0.005 %, high toughness is expected at the cooling rate as low as 2×10^{-2} K/s.

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