Effect of Austenite Grain Size on Sulfide Stress Cracking Resistance of Low Alloy Martensitic Steels

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Effect of grain size on sulfide stress cracking (SSC) resistance, thought to be an important metallurgical factor, is not clearly understood. There are some conflicting experimental results about grain size effect on SSC resistance. In this paper, effect of austenite grain size of low alloy tempered martensite steel was investigated using a constant load SSC test, considering their correlation with chemical compositions. An R_s value (SSC threshold stress/yield strength) begins to decrease with increase in yield strength at the yield strength equal to σ_c^{85} . Fractographic study reveals that σ_c^{85} corresponds to the minimum yield strength for the occurrence of intergranular fracture. σ_c^{85} rises with refinement in austenite grains, while R_s is not affected by austenite grain size at yield strengths below σ_c^{85} . σ_c^{85} at a constant grain size is influenced also by chemical compositions. When R_s is plotted against its tensile strength, no effect of austenite grain size, however, appears. The proposed model shows that grain refinement strengthening apparently increases σ_c^{85} .

KEY WORDS: sulfide stress cracking; low alloy steel; austenite grain size.

1. Introduction

Increasing demand of deep sour wells requires high strength tubulars with good resistance to sulfide stress cracking (SSC). SSC is a phenomenon of particular concern to oil and gas producers and refiners whose high strength drill pipes, production tubulars and other steel equipment can be subjected to failure when in contact with acid brines containing hydrogen sulfide (H_2S).¹⁾ Extensive research concerning SSC has been performed and has made it clear that SSC is a manifestation of hydrogen embrittlement. During the research, correlations between SSC resistance and metallurgical factors, particularly alloy effects, have been made clear to some extent, resulting in a successful development of high strength SSC resistant tubulars with specified minimum yield strengths of 90 ksi (617 MPa) and 95 ksi (652 MPa).^{2–6)} Further intensive metallurgical research on SSC made it possible to develop high strength SSC resistant tubulars with specified minimum yield strengths of 100 ksi (686 MPa) and 105 ksi (720 MPa).⁷⁾ However, metallurgical factors controlling SSC resistance still have not been fully understood. Among them, the ef-

fect of austenite grain size is not clear, though it has been investigated because hydrogen embrittlement of high strength steel occurs accompanying intergranular cracks. There are still conflicting observed results in the literature.^{8,9)}

The principal purpose of the present investigation is to understand the influence of the austenite grain size of low alloy tempered martensite steels on the SSC considering their correlation with chemical compositions.

2. Experimental Procedure

2.1. Materials and Heat Treatment

All heats of steels used in this study were melted in a vacuum induction furnace and cast into 50 or 100 kg ingots. The chemical compositions are listed in Table 1. Mn and Mo vary in content while the other elements are substantially the same in content. The ingots were cut in two along the middle plane of the section so as to avoid the influence of center segregation. The cut ingot were heated at 1523 K (1250°C) for 1 h, subsequently hot rolled to 12 to 14 mm thick plate. The austenite grain size was varied by changing austenitizing conditions.

Table 1. Chemical compositions of steels. (wt%)

Steel	C	Si	Mn	P*	S*	Cr	Mo	Nb	Al	Ti	N*	B*
HC	0.20	0.05	1.46	120	10	0.49	—	—	0.028	0.018	39	8
HM	0.19	0.06	1.47	120	20	0.52	0.20	—	0.029	0.020	40	6
LM	0.20	0.05	0.51	130	10	0.51	0.20	—	0.026	0.019	30	14

* [ppm].

The plates were austenitized at 1203 K (930°C) to 1423 K (1150°C) for 30 sec or 15 min, followed by quenching into stirring water. Because every steel used here has enough hardenability, the quenched steel was transformed into full martensite. Then the steels were tempered at various temperatures, followed by water cooling. A salt bath was used for 30 or 60 sec heating while a conventional electric furnace was used for longer heating times.

2.2. Measurement of SSC Resistance

The constant load SSC test according to the NACE TM0177-90A¹⁰⁾ was conducted to evaluate SSC resistance of steel. Smooth round bars with 6.4 mm diameter shown in Fig. 1 were machined in the rolling direction after the heat treatment. The tests were performed using dead weight testers, and in the NACE TM0177 solution (0.5%CH₃COOH + 5%NaCl solution saturated with 1 atm H₂S). The solution volume of specimen surface area was 30 ml/cm² and the test temperature was 24 ± 3°C. The maximum initial stress at which no failure occurs during the test period of 720 h is a threshold stress (σ_{th}), which is adopted as an SSC resistance value. An R_s value, a σ_{th} normalized by the yield strength is also used.

2.3. Fractographic Observation of SSC

It was difficult to observe microscopically the fracture surface of the specimens subjected to the constant load test because the fracture surface was exposed to the corrosive solution after the failure and damaged due to corrosion. Therefore the constant load tester was equipped with a device which protected the fracture

Fig. 1. Constant load SSC test specimen.

surface from the corrosion. Immediately after the test specimen failure, supply of H₂S gas is stopped. Then the corrosive solution is discharged and alcohol is put into the vessel. This liquid substitution is repeated twice. The process automatically starts by sensing the failure. Thus the fresh fracture surface can be obtained. After pickling the specimen in 10% H₂SO₄ solution with an inhibitor, an SSC fracture surface was examined with a scanning electron microscope (SEM).

3. Experimental Results

3.1. Microstructure and Mechanical Properties

Examples of prior austenite grains are presented in Fig. 2. Austenite grain size becomes coarse with an increase in austenitizing temperature and prolongation in austenitizing time as shown in Fig. 3. Change of properties with tempering temperature is represented in Fig. 4 for the steel HC; yield strength and tensile strength gradually decrease with increase in tempering temperature. At a constant tempering temperature, yield strength for the finer grains is higher than that for the coarser grains, though little influence on tensile strength exists.

Figure 5 represents extraction replica micrographs of the steels with the same chemical composition, the same strength level and different grain sizes. No particular difference in the size and the distribution of carbides can be observed.

3.2. Effect of Austenite Grain Size on SSC Resistance

In Fig. 4, SSC resistance, R_s rises up to 0.9 level with increase in tempering temperature. The experimental data in Fig. 4 are replotted in Fig. 6 to see the relation between R_s and yield strength. At lower yield strengths, R_s values are saturated to a value of 0.9 or so, where no effect of grain size is observed. With increase in yield strength, R_s begins to decrease at a certain yield strength. Here, the yield strength where R_s corresponds to 0.85 is named as an SSC critical strength (σ_c^{85}); R_s is lower than 0.85 at yield strengths exceeding the yield strength equal to σ_c^{85} . σ_c^{85} is influenced by the grain size and becomes large with grain refinement. R_s , however, is not influenced by the grain size at yield strengths below σ_c^{85} . Namely,

Fig. 2. Examples of prior austenite grains. (steel LM)
(A) 930°C × 15 min, (B) 1050°C × 15 min.

the σ_c^{85} represents SSC resistance for each quenched steel.

The experimental data for the steel HM and LM obtained in the same procedure above mentioned are presented in Fig. 7 and Fig. 8, respectively. The relations between yield strength and R_s are similar to that of Fig. 6.

The results presented in Figs. 6, 7 and 8 are arranged in Fig. 9. It shows the change of σ_c^{85} as the function of austenite grain size. σ_c^{85} rises as austenite grain becomes small for steel with a given chemical composition. At a constant grain size, σ_c^{85} is also affected by chemical compositions; an addition of Mo raises σ_c^{85} by around 20 MPa and a reduction of 1% of Mn raises σ_c^{85} by around 70 MPa. It should be noted that the microstructures of steels in this study are tempered martensite and substantially the same, irrespective of chemical composition and grain size.

3.3. Fractographic Observation of SSC Surface

A fracture surface macroscopically consists of SSC surface and ductile fracture surface. The former is flat and perpendicular to the stress direction and the latter is the final portion of failure. Microscopic features of fracture surface of a specimen is the same in all of SSC surface. Scanning electron micrographs of typical SSC

surfaces are shown in Fig. 10. Figures 10A, 10D, 10E are examples of transgranular fracture surfaces. Figures 10B, 10C, 10F are examples of mixture of intergranular and transgranular cracks. Steels with high R_s of 0.9 level shows transgranular fractures, while intergranular cracks appear in steels with lower R_s , irrespective of chemical composition, grain size and yield strength. For example, Figs. 10B and 10D are fracture surfaces of steels which are different only in grain size. Fine grained steel (Fig. 10D) with R_s of 0.95 shows fully transgranular fracture, while coarse grained steel (Fig. 10B) with R_s of 0.77 shows fracture containing intergranular cracks. Thus, intergranular cracks appear when R_s is below 0.9 level. These observations show that intergranular cracks oc-

Fig. 3. Change of austenite grain size by austenitizing conditions.

Fig. 4. Dependence of YS, TS and R_s on tempering temperature.

Fig. 5.

Extraction replica micrographs of steel HC with the same strength level and different grain size.

(A) G.S. No.: 8.3, YS: 716 MPa, (B) G.S. No.: 5.0, YS: 697 MPa.

 Fig. 6. Relation between yield strength and R_s value. (1.5%Mn-0%Mo)

 Fig. 8. Relation between yield strength and R_s value. (0.5%Mn-0.2%Mo)

 Fig. 7. Relation between yield strength and R_s value. (1.5%Mn-0.2%Mo)

 Fig. 9. Effects of austenite grain size and chemical compositions on σ_c^{85} .

cur at yield strengths exceeding σ_c^{85} . It is clear that the R_s value decreases due to an occurrence of intergranular cracks, irrespective of chemical composition and grain size.

4. Discussion

R_s value, a normalized σ_{th} by the yield strength begins to decrease with increase in yield strength at the yield strength equal to σ_c^{85} . σ_c^{85} rises with refinement of austenite grain size, also being influenced by chemical compositions as shown in Fig. 9. The fractographic observation reveals that σ_c^{85} corresponds to the minimum yield strength for the occurrence of intergranular cracks as mentioned previously by the authors.¹¹⁾

A change of σ_c^{85} is easily supposed to be caused by a change in grain boundary strength, which is probably influenced by grain boundary segregation or grain boundary precipitation or the both. Changes of Mn and Mo in content presumably change the both factors, leading to the change in σ_c^{85} . Then, the mechanism of grain size on σ_c^{85} will be discussed below.

First, the size and distribution of precipitates along

grain boundaries are substantially the same for fine and coarse grains as shown in Fig. 5. Second, the amount of segregation on grain boundaries is supposed to be not affected by grain size. The reason is shown as follows. Assuming that grain boundary segregation follows the McLean's equilibrium model,¹²⁾ the concentration of a solute atom on grain boundaries is expressed by Eq. (1).

$$X_b/(X_b^0 - X_b) = X_c/(1 - X_c) \exp(Q/kT) \quad \dots\dots\dots(1)$$

where, X_b : concentration of a solute atom on grain boundaries,

X_b^0 : saturation concentration of a solute atom on grain boundaries,

X_c : concentration of a solute atom in grains,

Q : difference of free energy of a solute atom between on grain boundaries and in grains.

As far as a grain boundary structure does not vary by a change of grain size, Q is thought to be a constant, irrespective of grain size. Therefore X_b is uniquely determined by X_c , which is almost a constant regardless of grain size as easily shown in the following calculation.

$$X = X_c(1 - S_v t) + X_b S_v t \quad \dots\dots\dots(2)$$

Fig. 10. Scanning electron micrographs of typical SSC surfaces.

(Steel, Grain size No., YS, R_s)

(A) LM, #4.9, 742 MPa, 0.91 (B) LM, #4.9, 767 MPa, 0.77 (C) LM, #4.3, 829 MPa, 0.35

(D) LM, #8.5, 769 MPa, 0.95 (E) HC, #9.3, 707 MPa, 0.95 (F) HC, #9.3, 780 MPa, 0.60

where, X : average concentration of a solute atom of a material,

S_v : grain boundary surface area under the normalizing condition that the average grain volume is a unit volume,

t : grain boundary thickness.

Considering $S_v t$ is small, the equation can be rewritten as follows:

$$X_c = X / (1 + (X_b/X_c) S_v t) \quad \dots \dots \dots (3)$$

Now it can be reasonably estimated that S_v is about $3/r$ where r is a grain radius, t is 1 nm and (X_b/X_c) is at most 100,¹³⁾ and that the difference of X_c between for r of 10 μm and for r of 100 μm is 3% or so. Therefore, the change of a concentration of grain boundary segregation due to grain size change is regarded to be negligible small.

As shown in Fig. 4, a tempering temperature where R_s starts to decline is equal for any grain sizes. This suggests that intergranular fracture occurs at a constant tempering temperature, that is, at a constant segregation concentration regardless of grain size. However, yield strength at a constant tempering temperature rises with a reduction in grain size due to grain refinement strengthening. Thus, σ_c^{85} of fine grain steel increases. When R_s is plotted as a function of tensile strength which little depends on grain size, all data are actually on a simple relationship (Fig. 11). In conclusion, the following

Fig. 11. Relation between tensile strength and R_s .

model is presented: A change in σ_c^{85} is primarily caused by a rise in yield strength due to grain refining strengthening under a constant grain boundary strength condition.

5. Conclusions

Effects of austenite grain size on SSC resistance were investigated using the constant load SSC test and the

fractographic observation technique on SSC surface for low alloy tempered martensite steels with the variation in Mn and Mo contents. The important conclusions drawn from the present work are as follows:

(1) R_s value (σ_{th} /yield strength) begins to decrease with increase in yield strength at the yield strength equal to σ_c^{85} . σ_c^{85} corresponds to the minimum yield strength for the occurrence of intergranular fracture.

(2) σ_c^{85} rises with refinement in austenite grains, while R_s is not affected by austenite grain size at yield strengths below σ_c^{85} . σ_c^{85} at a constant grain size is influenced by chemical compositions; σ_c^{85} is lowered by an increase in Mn and is raised by an addition of Mo.

(3) The model which can explain the present experimental relations for the effect of austenite grain size on σ_c^{85} is as follows: An increase in σ_c^{85} with grain refinement is primarily caused by a rise in yield strength due to grain refinement strengthening under a constant grain boundary strength condition.

REFERENCES

- 1) R. S. Treseder: Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, ed. by R. W. Staehle, J. Hockmann, R. D. McCright and J. E. Slater, NACE, Houston, (1977), 147.
- 2) T. Sato, H. Higashiyama, K. Yamamoto, T. Inoue and M. Ueno: Proc. of Offshore Technology Conf., (1989), Paper No. 4331.
- 3) A. Ikeda, S. Nagata, T. Tsumura, Y. Nara and M. Kowaka: Symposium on Line Pipe and Tubular Goods at the API Production Dept., 1977 Standardization Conference, Florida, (1977), No. SS-5: 1.
- 4) M. Tanimura, Y. Ishizawa and T. Simada: *Corros. Prev. Control*, Feb. (1984), 5.
- 5) C. D. Kim and F. Baldy: Proc. of 8th ETCE, ASTM, (1985), 83.
- 6) F. R. David, G. C. Guntz and M. F. J. Galis: *Corrosion/89*, NACE, (1989), Paper No. 474.
- 7) H. Asahi, Y. Sogo, M. Ueno and H. Higashiyama: *Corrosion*, **45** (1989), 519.
- 8) R. P. M. Proctor and H. W. Paxton: *Trans. Am. Soc. Met.*, **62** (1969), 989.
- 9) J. F. Lessar and W. W. Gerberich: *Metall. Trans. A*, **7A** (1976), 953.
- 10) NACE Standard TM0177-90, NACE, Houston, (1990).
- 11) H. Asahi, Y. Sogo, M. Ueno and H. Higashiyama: *Metall. Trans. A*, **19A** (1988), 2171.
- 12) D. Mclean: *Grain Boundaries in Metals*, Oxford Univ. Press, (1957), 116.
- 13) K. Tatsumi, N. Okumura and M. Yamamoto: *J. Phys., Colloque*, Interface Sci. Eng. '87, (1988), C5-699.