

IMPROVEMENT OF HYDROGEN EMBRITTLEMENT IN A TEMPERED MARTENSITIC STEEL THROUGH GRAIN REFINEMENT USING UNDISSOLUBED CEMENTITE

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ABSTRACT

The influence of the grain size of the prior-austenite on the hydrogen-induced delayed fracture property was investigated for a medium-carbon tempered martensitic steel (JIS-SCM440) with a tensile strength of 1400MPa. Thermomechanical processing, which consists of a warm working at 873K by multi-pass bar rolling of tempered martensite and subsequent rapid austenitizing at 1093-1123K, resulted in the refinement of the prior-austenite grain to 3 μm . The hydrogen embrittlement susceptibility of the steels was evaluated by means of a constant loading test, a slow strain rate test and a hydrogen immersion test. It was confirmed that the grain refinement using undissolved cementite was effective for improving the hydrogen-induced delayed fracture property compared to the conventional QT steel (prior-austenite grain size; 11-17 μm) at the tensile strength of 1400MPa, where intergranular fracture took place.

KEYWORDS

High-strength steel, medium-carbon low-alloy steel, thermomechanical processing, tempered martensite, prior-austenite, grain refinement, hydrogen embrittlement

INTRODUCTION

High-strength low-alloy steels are generally susceptible to hydrogen embrittlement in the tensile strength over 1200MPa and this usually restricts practical use of high-strength steels. The attempts as follows are considered to be effective to improve the susceptibility to hydrogen embrittlement;

- (1) Increase of intrinsic fracture resistance
- (2) Suppression of hydrogen accumulation to crack initiation sites and crack tips by utilizing effective hydrogen trapping sites such as nanosize carbides[1], etc.
- (3) Decrease of hydrogen intrusion from a circumstance.

In many cases, the hydrogen-induced delayed fracture of tempered martensitic steel occurs along the grain boundaries of the prior-austenite. Hence, the resistance to the hydrogen embrittlement can be improved by controlling the prior-austenite grain size, the grain boundary structure which involves grain boundary carbides, segregated impurities, etc, and the texture. Recently, Tarui et al. [2,3] reported that hydrogen embrittlement susceptibility was improved by direct quenching from work hardened austenite, the so-called modified ausforming [4], in a 0.29%C boron steel and a

0.35% C-Cr-Mo steel with a tensile strength of 1450 MPa, and intergranular fracture was suppressed in the thermomechanically processed samples. Some of the present authors showed similar results in a 0.4% C-Cr-Mo steels with a tensile strength of 1450 MPa [5,6]. The improvement in the hydrogen embrittlement susceptibility is thought to be due to the refinement in grain boundary cementite [6] and the development of texture [7] through the ausforming treatments.

Grain refinement is especially important method not only for the strengthening of steels but also for improving the fracture properties because the intergranular fracture can be suppressed by the following effects of grain refinement;

- (1) Reduction in stress concentration at the grain boundaries,
- (2) Reduction in the degree of segregated impurities at the grain boundaries because of the increase in the grain boundary area per unit volume with grain refining.

Several researchers [8-13] have investigated the influence of the prior-austenite grain size on the hydrogen-induced delayed fracture. However, there are conflicting results in the reports with respect to the role of the prior-austenite grain size. Differences may arise because of the different microstructures (undissolved carbide, retained austenite, grain boundary structure, etc.) that are obtained in the effort to vary grain size. Besides, only a few studies have been carried out for fine-grained steels with a prior-austenite grain size of a few μm or less, in which “the grain refinement effects” are expected to become significantly larger.

The aim of this study is to investigate the influence of the prior-austenite grain refinement on the hydrogen-induced delayed fracture property for a medium-carbon tempered martensitic steel. Thermomechanical processing, which consists of a warm working of tempered martensite and subsequent rapid austenitizing [14] was applied to obtain finer austenite grains. In this treatment, we intend to utilize undissolved carbides not only to refine the austenite grains but also to suppress the formation of film-like coarse cementite particles, which usually cause failure. Special attention was also given to the distribution state of undissolved carbides and their influence on mechanical properties.

EXPERIMENTAL

A commercial medium-carbon alloy steel (JIS-SCM440) with a chemical composition of 0.40% C, 0.21% Si, 0.81% Mn, 0.02% P, 0.01% S, 1.03% Cr, 0.16% Mo, and the balance Fe (mass%) was used. A martensitic billet with a diameter of 40 mm was tempered at 873K for 5.4ks and was subjected to multi-pass bar rolling into a 12mm square bar. Then, the sample was rapidly austenitized at 1093-1123K, followed by water-quenching with an induction heating device to refine the prior-austenite grains. A conventional quenched and tempered specimen was also prepared for reference. The normalized bar was austenitized at 1153K for 1.8ks and then was oil-quenched. These martensitic specimens were tempered at 723K and 873K for 5.4ks, and were water-quenched. The hydrogen-induced delayed fracture properties were examined for the samples that were machined after tempering. The hydrogen embrittlement susceptibility was examined for the hydrogen pre-charged notched samples by a constant load test (CLT) [15] and a slow strain rate test (SSRT) [16]. The stress concentration factor of the samples was 4.9. The hydrogen was electrically charged with a 3% NaCl+0.3% NH₄SCN water solution or a 0.1N NaOH aqueous solution. The

hydrogen content was altered by controlling the current density and charging time. The hydrogen charged samples were electrically coated with Cd to avoid the evolution of hydrogen and kept at an ambient temperature for 24 h to obtain a uniform hydrogen content profile within the sample before loading. For the CLT, the constant load was applied to samples with a conventional creep test machine. The apparent applied stress on the minimum cross section area was 0.9 TS, where TS is the tensile strength of the un-notched samples. The SSRT was carried out on a shimazu AG-250kNI tensile testing machine with a constant crosshead speed of 0.005mm/min, corresponding to a nominal strain rate of $8.3 \times 10^{-7} \text{ s}^{-1}$. After failure, the samples were kept at liquid nitrogen temperature until thermal desorption spectrometry analysis of the hydrogen was carried out. For the hydrogen immersion test, samples with a diameter of 5 mm and a length of 30mm were machined, and then were kept in a 0.1M HCl water solution (pH=1.0) at 298K for various times. The average hydrogen content of the samples after the completion of these tests was measured by means of the thermal desorption spectrometry analysis with a quadrupole spectrometer (Q-mass). The heating rate of the samples was 100K/h and the total hydrogen content that was released up to 573K was defined as the diffusible hydrogen content that causes the delayed failure.

RESULTS AND DISCUSSION

Figure 1 shows carbide structures of the sample that was bar-rolled at 873K (a) and then was rapidly austenitized for 1093K for 3s (b). Spheroidized microstructure was formed through the warm rolling of a tempered martensitic structure. The average diameter of the cementite is $0.07 \mu\text{m}$, and the carbide distribution is relatively uniform. When the rolled sample was rapidly austenitized, undissolved carbides existed in the as-quenched state. The maximum diameter of the undissolved carbides was $0.25 \mu\text{m}$ and approximately agreed with that of cementite in the bar-rolled sample. These undissolved carbides are believed to retard the growth of the austenite by the pinning effect. As a result, fine austenitic grain structure with the average grain size of $3 \mu\text{m}$ was obtained in the thermomechanically processed samples.

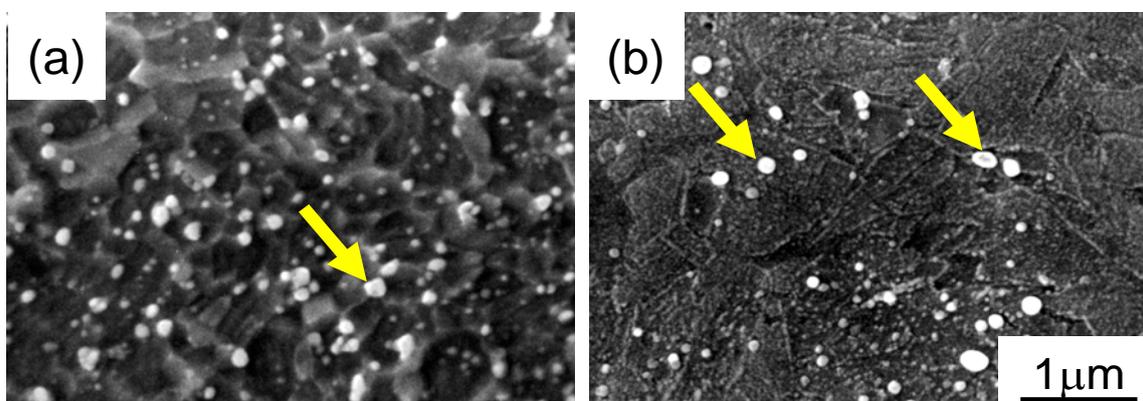


Fig. 1 SEM micrographs showing the carbide structures of the sample that was rolled at 873K (a) and then was rapidly austenitized at 1093K for 3s (b). The arrows indicate carbide particles

Figure 2 shows the tempered martensitic structures of the fine-grained sample (a) and the conventional QT sample (b) after tempering at 723K. Coarse film-like grain boundary carbides that were several μm in length were observed in the conventional QT sample (the average prior-austenite grain size; $11\mu\text{m}$) as indicated by the arrow in Fig.2 (b). On the other hand, coarse grain boundary carbide plates were not formed in the fine-grained sample with spherical undissolved carbides. This is due to the existence of the undissolved carbides at the grain boundary before tempering. When undissolved carbides exist on the grain boundary, the growth of such pre-existing carbides predominantly occurs rather than the precipitation of new carbides on the grain boundary during tempering.

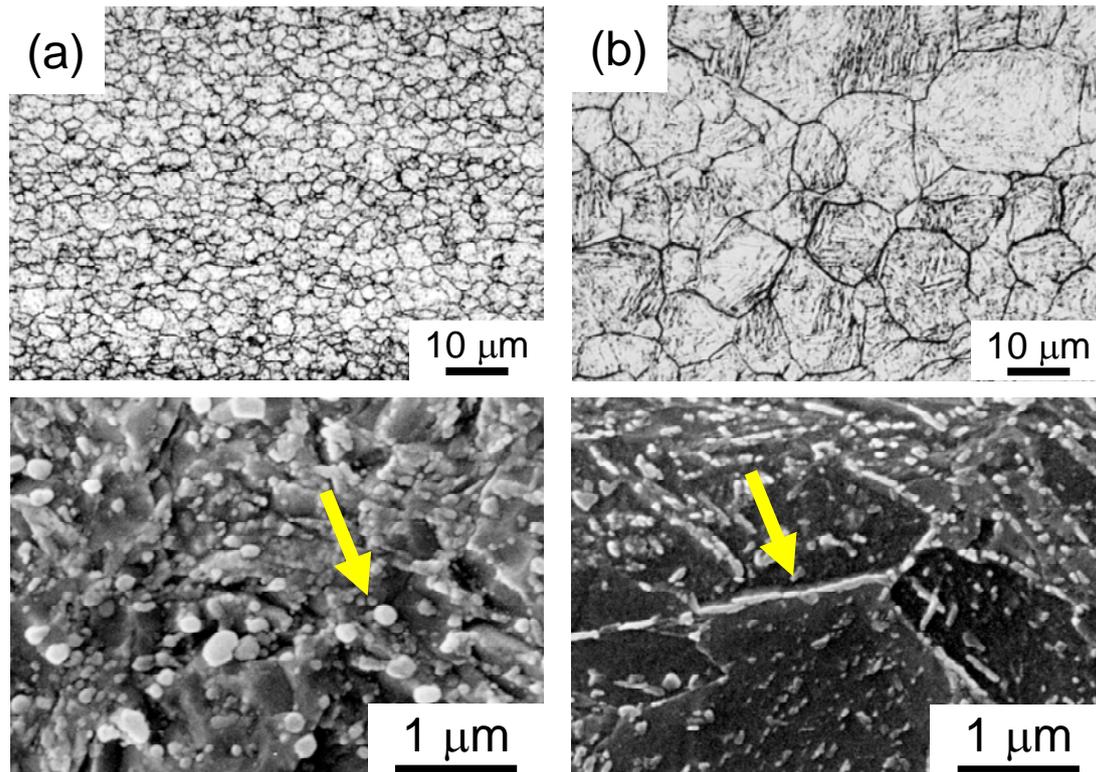


Fig. 2 Tempered martensitic structures of fine-grained sample (a) and conventional QT sample(b) after tempering at 723K for 5.6ks. The arrows indicate grain boundary carbides.

Tensile properties of the steels that were tempered at 723K and 873K are listed in Table 1. The 0.2% proof stress of the fine-grained samples was higher than that of the conventional QT samples in the same tempering temperature, but the other tensile properties were almost the same. Comparable values for the reduction in area (61% and 58%) suggested that spherical undissolved carbide particles with a diameter of less than $0.25\mu\text{m}$ were not harmful for ductility even at the tensile strength level of 1400MPa.

Table 1 Tensile properties of fine-grained samples ($D\gamma=3\mu\text{m}$) and conventional QT samples ($D\gamma=11\mu\text{m}$).

Steel	$\sigma_{0.2}$ (MPa)	σ_B (MPa)	Eu (%)	Et (%)	R.A.(%)
$11\mu\text{m}$ (723K)	1303	1430	3.7	12.6	58
$3\mu\text{m}$ (723K)	1376	1397	3.6	12.7	61
$11\mu\text{m}$ (873K)	906	1019	6.8	18.0	67
$3\mu\text{m}$ (873K)	953	994	6.5	18.6	67

Figure 3 shows the relations between the diffusible hydrogen content and the time to failure for the fine-grained sample and the conventional QT sample that were tempered at 723K for 5.4ks[17]. In both samples the time to failure increased as the diffusible hydrogen content decreased. The critical diffusible hydrogen content (H_c), below which the fracture never took place, was 0.11 ppm for the conventional QT sample. On the other hand, the critical value increased to 0.24 ppm for the fine-grained sample. Figure 4 shows the dependence of notch tensile strength on diffusible hydrogen content for the samples that were tempered at 723K and 873K. All the hydrogen charged samples showed a lower notch tensile strength than those of the uncharged samples, indicating a hydrogen embrittlement of the steel. The samples that were tempered at 873K showed gradual decreases in the notch tensile strength with increasing the diffusible hydrogen content, but the notch tensile strength of these samples was much higher than their tensile strength of 1000MPa in the present hydrogen content range. Hence the 1000MPa-class high strength steels had high resistance to hydrogen embrittlement. On the other hand, the notch tensile strength of the samples that were tempered at 723K decreased abruptly in the low hydrogen content region, and was lower than 800MPa when the hydrogen content was around 0.5 ppm. The notch tensile strength of the fine-grained samples was, however, higher than that of the QT samples in the whole hydrogen content, corresponding to the result in the Fig.3.

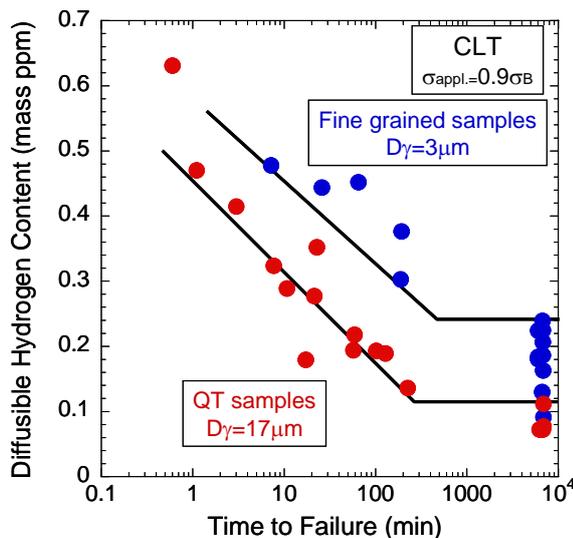


Fig. 3 Relations between the diffusible hydrogen content and the time to failure for fine-grained sample ($D\gamma=3\mu\text{m}$) and conventional QT sample ($D\gamma=17\mu\text{m}$) tempered at 723K for 5.4ks [17].

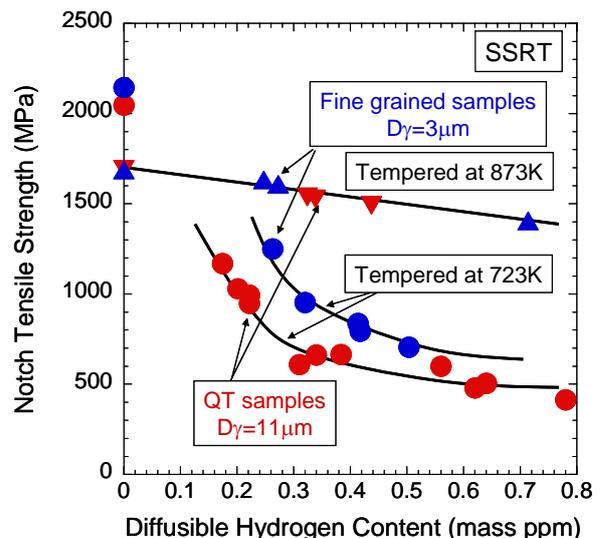


Fig.4 Relations between the notch tensile strength and the diffusible hydrogen content for fine-grained sample ($D\gamma=3\mu\text{m}$) and conventional QT sample ($D\gamma=11\mu\text{m}$) tempered at 723K and 873K for 5.4ks.

Figure 5 shows SEM fractographs taken from the crack initiation regions in the vicinity of the notch-root in the fine-grained (a) and the QT (b) samples that were tempered at 723K and then were subjected to the SSRT with diffusible hydrogen content of about 0.5ppm. The fracture

surfaces of the samples that were tempered at 873K was characterized by quasi-cleavage, while the intergranular fractures were observed in both of the fine-grained and the QT samples after the tempering at 723K. However the area of intergranular fracture was smaller than 10 μm for the fine-grained sample and significantly reduced compared to that of the conventional QT sample (Fig.5(b)). Concerning hydrogen intrusion, the intruded hydrogen content (HE) was 0.14 ppm for the fine-grained sample after the 360ks immersion test in a 0.1M HCl water solution (pH=1.0) at 298K and almost the same as that of the conventional QT sample (0.17 ppm)[17]. From the results, it might be concluded that the grain refinement of the prior-austenite to 3 μm was not enough to entirely suppress the intergranular fracture, but was effective for improving the hydrogen-induced delayed fracture property at the tensile strength of 1400MPa, where the intergranular fracture occurred. The additional effects of hydrogen trapping, texture, etc. to the grain refinement might thus lead to raising the resistance to hydrogen embrittlement susceptibility significantly.

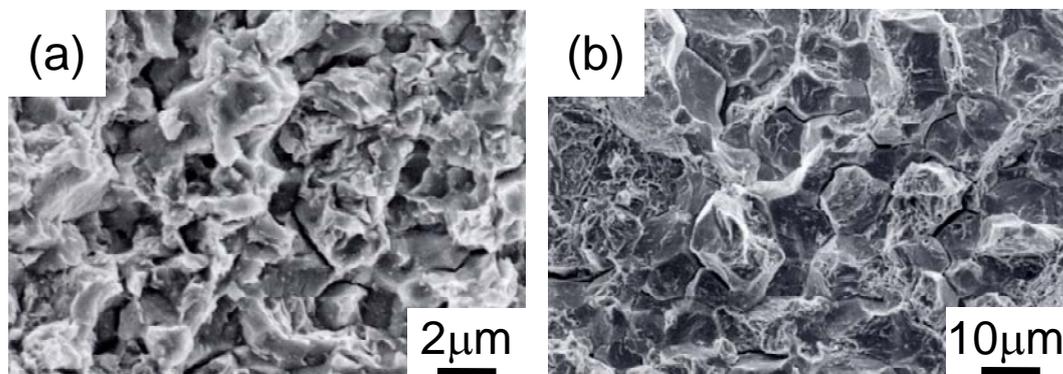


Fig. 5 SEM fractographs taken from the crack initiation regions in the fractured samples; (a) fine-grained sample ($D\gamma=3\mu\text{m}$) and (b) conventional QT sample ($D\gamma=11\mu\text{m}$).

CONCLUSIONS

- (1) Thermomechanical processing, which consists of a warm working at 873K by multi-pass bar rolling of tempered martensite and subsequent rapid austenitizing at 1093-1123K, resulted in a homogeneous distribution of fine undissolved carbides and the refinement of the prior-austenite grain to 3 μm
- (2) Undissolved carbide particles with a diameter of less than 0.25 μm are not harmful for ductility at the tensile strength of 1400MPa.
- (3) The grain refinement of the prior-austenite to 3 μm using undissolved carbide was effective for improving the hydrogen-induced delayed fracture property compared to that of the conventional QT steel (prior-austenite grain size; 11-17 μm) at the tensile strength of 1400MPa, where intergranular fracture took place.

REFERENCES

- 1) E.G.WEI, T.HARA, K.TSUZAKI, Metall.Mater.Trans.B 35B, (2004), p.587.
- 2) T.TARUI, S.YAMASAKI, M.TATEYAMA, T.TAKAHASHI and Y.NOGUCHI, CAMP-ISIJ, 10, (1997), p.1291.
- 3) S.YAMASAKI, T.TARUI and Y.NOGUCHI, CAMP-ISIJ, 11, (1998), p.1242.
- 4) R.A.BOOCK and W.M.JUSTUSSON, Metal Progress, 94, December, (1968), p.107.
- 5) S.YUSA, T.HARA, K.TSUZAKI, T.TAKAHASHI, Y.NOGUCHI and K.KAWASAKI, CAMP-ISIJ, 12 (1999), p.565.
- 6) S.YUSA, T.HARA, K.TSUZAKI and T.TAKAHASHI, CAMP-ISIJ, 12 (1999), p.1296.
- 7) T.TARUI, D.HIRAKAMI, S.YAMASAKI, N.MARUYAMA, M.KUBOTA, CAMP-ISIJ, 12, (1999), p.1045.
- 8) R.P.M.PROCTER, H.W.PAXTON, Trans. ASM, 62 (1969), p.989.
- 9) S.MATSUYAMA, Tetsu-to-Hagane, 58 (1972), p.395.
- 10) J.F.LESSAR, W.W.GERBERICH, Met. Trans., 7A, (1976), p.953.
- 11) S.K.BANERJI, Jr.C.J.McMAHON, H.C.FENG, Met. Trans., 9A, (1978) pp.237-247.
- 12) R.PADMANABHAN, W.E.WOOD, Met. Trans., 14A, (1983), p.2347.
- 13) W.J.HUI, H.DONG, S.L.CHEN, M.Q.WANG, Y.Q.WENG, Proc. Inter. Symp. Ultrafine Grained Steels, Fukuoka 20-22 September 2001, edited by S.Takaki and T.Maki (Iron and Steel Inst.Japan, Tokyo, 2001) p.232.
- 14) M.TORKIZANE, K.AMEYAMA, K.TAKAO, Scripta Metall., 22, (1988) ,p.697.
- 15) S.YAMASAKI, T.TAKAHASHI, Tetsu-to-Hagane, 83, (1997) , p.454.
- 16) M.WANG, E.AKIYAMA and K.TSUZAKI, Mater. Sci. Eng.A, 398 , (2005), p.37.
- 17) Y.KIMURA, S.TAKAGI, T.HARA, S.TERASAKI, K.TSUZAKI, Journal de Physique IV-Proceedings France 112, (2003), p.403.