Effects of Heat-treatment Process of a Novel Bainite/Martensite Dual-phase High Strength Steel on Its Susceptibility to Hydrogen Embrittlement

Kai-Di CHANG, Jia-Lin GU, Hong-Sheng FANG, Zhi-Gang YANG, Bing-Zhe BAI and Wen-Zheng ZHANG

Department of Materials Science and Engineering, Tsinghua University, Beijing, 100084, P. R. China.
E-mail: changkd@263.net

(Received on May 1, 2001; accepted in final form on June 25, 2001)

The susceptibility to hydrogen embrittlement of a bainite/martensite dual-phase high strength steel with different morphologies obtained by the conventional or thermomechanical heat-treatment has been investigated by means of electrolytic hydrogen charging in this paper. The results show that the finer the microstructure, the lower the sensitivity of steel to hydrogen embrittlement is. The fractographic analysis suggests that the fracture mode of the hydrogen-charged specimens is a mixture of quasicleavage and dimple for both treating processes. The quasicleavage facet of the thermomechanical treated specimens is smaller than that of the conventional heated ones. The observation of the fracture profile specimen shows that the crack propagates preferentially along bainite/martensite laths boundary, suggesting that the fracture mode is predominantly lath boundary separation. In addition, the fractographic analysis indicates that the rhombic Ti(N,C) inclusion is the predominant type of inclusions on the fracture surface of the hydrogen-charged specimens of thermomechanical heat-treatment. The separation between Ti(N,C) inclusions and matrixes is a brittle fracture with small facets, which indicates that inclusions such as Ti(N,C) are harmful to hydrogen embrittlement.

KEY WORDS: bainite/martensite dual-phase steel; hydrogen embrittlement; thermomechanical treatment.

1. Introduction

It is very imperative to study the novel high strength steels with high purity, high uniformity and fined grain in order to improve properties to meet the needs of usages. However, the increase of strength of steel will decrease its resistance to hydrogen embrittlement (HE). For example, in last century, some hydrogen embrittlements in the landing gear of plane were reported. In 1970–1980, study of HE became more and more popular. High strength steels being used now, yield strength exceeding 1380 MPa, exhibit strong susceptibility to HE. There are many variables affecting the HE of steels, such as strength, composition and microstructure.

The effect of microstructure on the resistance to HE is more directly than that of strength. There are many works with respect to different microstructure effects. In general, the susceptibility of the materials with martensite is more severe than ones with pearlite and austenite. Xu pointed out that the embrittlement index of materials with various microstructures in the order of reduction as follows: martensite→troostite→sorbite→ferrite→pearlite. Recently, study of HE for the steels with ultra-purity, ultra-cleanliness, and ultra-refinement has attracted some attentions. Refinement of grain can not only improve strength and ductility, however, the literature on study of hydrogen embrittlement for bainite/martensite dual-phase microstructure is quite sparse. Therefore, this work is to study the effects of fined bainite/martensite dual-phase microstructure gained by thermomechanical heat-treatment on HE, which is valuable for development of a novel high strength steel.

2. Experimental Procedure

The materials investigated were made by vacuum-induction melting, whose compositions are given as follows: in weight percent, Fe–1.8Mn–1.3Si–0.3Cr–0.01Ti–0.27C–0.009S–0.007P. The details of the heat treatment are shown in Table 1.

In the tensile tests, standard short gauge specimens with a diameter of φ6.4 mm are used. Several specimens were cathodically charged with hydrogen in current density of 0.2, 0.5, 0.7, 0.9, 1 mA/cm² for four hours in an aqueous solution of 5% H₂SO₄ containing 250 mg/l As₂O₃ as a hydrogen recombination poison. The specimens were then subject to tensile testing after being aged for half an hour. According to literature, the present hydrogen charging conditions are relatively severe. Tensile tests were conducted at room temperature in a strain rate of 0.5 mm/min with Japan Instron AG 75TA universal electron testing machine. Microstructure of the specimen and the fractography of ten-
sile specimen were observed by OPTON CSM950 scanning electron microscope (SEM) and transmission electron microscope (TEM). The volume percentages of retained austenite in the materials investigated were assessed using D/MAX-RB X-ray diffraction apparatus.

### 3. Experimental Results

The original microstructure for two heat treatments is shown in Fig. 1, which is bainite/martensite dual-phase microstructure, there also are a few retained austenites whose volume percent is shown in Table 1. Bainite/martensite lath sizes change from 10 to 5 μm in length and 0.7 to 0.6 μm in width in the specimens of conventional heat-treatment and thermomechanical heat-treatment. Thermomechanical heat–treatment refines bainite/martensite dual-phase microstructure evidently.

The microstructure of the specimen of thermomechanical heat-treatment is illustrated in Fig. 2 by TEM. The microstructure consists of martensite with high density dislocation and bainite with retained austenite films, and the retained austenite films appear within bainite and at the interfaces between the bainite plates and martensite lathes. Embrittlement index ($E_H$) is usually employed to assess the susceptibility to HE. $E_H$ is given by $E_H = (\psi_0 - \psi_H)/\psi_0 \times 100\%$, where $\psi_0$ and $\psi_H$ are reduction of area (RA) of hydrogen-uncharged and hydrogen-charged tensile specimens, respectively. The change of RA and $E_H$ vs. cathodic current density for two specimens with tensile strength of 1500 MPa is shown in Fig. 3. It can be seen that hydrogen charging decreases markedly the ductility of steels.

![Fig. 1. SEM micrographs for two heat-treatments: (a) conventional heat-treatment; (b) thermomechanical heat-treatment.](image)

![Fig. 2. TEM Images for thermomechanical heat-treatment: (a) bainite/martensite dual-phase microstructure with retained austenite; (b) magnified retained austenite dark field imaging corresponding to upper, cleft corner of (a). B: bainite, M: martensite, $\gamma_A$: retained austenite.](image)

| Specimen | Heat-treatment mode | Austenitizing temperature (K) | Holding time (min) | Cooling mode | Tempering temperature (K) | Volume of retained austenite (%) |
|----------|---------------------|-----------------------------|-------------------|-------------|---------------------------|---------------------------------|
| B        | Thermomechanical heat-treatment | 1133 | 18 (113K, hot-deformation true strain 30%, rate of strain $6 \times 10^{-5}$ s$^{-1}$) | Air cooling | 553 | 9 |
| C        | Conventional heat-treatment | 1173 | 10 | Air cooling | 553 | 6 |

Table 1. Processing parameters for two heat-treatments.
exhibits only slight decrease and its $E_H$ is very low, when cathodic current density is lower than 0.5 mA/cm$^2$. The susceptibility to HE of materials is sorted into three categories according to embrittlement index ($E_H$)\textsuperscript{15}). The $E_H$ below 25% is safe, and the $E_H$ over 35% is brittle. When cathodic current density $i \leq 0.5$ mA/cm$^2$, the $E_H$ of the steel for thermomechanical heat-treatment is only 15%, which is lower than 25%. Therefore, its susceptibility to HE is very low, whereas the steel of conventional heat-treatment exhibits very high susceptibility to HE, even when cathodic current density $i = 0.2$ mA/cm$^2$. The RA decreased significantly, and its $E_H$ is far larger than that of thermomechanical heat-treatment.

Figure 4 illustrate quasicleavage fracture morphology of both specimens with cathodic current density of $i = 0.2$ mA/cm$^2$ for four hours. Intergranular fracture has not been observed in the figures. Figure 4(a) shows the quasicleavage facets on the tensile fractography of the conventional heat-treatment are very large, in contrast, the quasicleavage facets on the tensile fractography of thermomechanical heat-treatment with same cathodic current density are very small, which correspond to the unit size of microstructure. However, tensile fractography of the hydrogen uncharged both specimens exhibits similar cup-cone dimple fracture.
Fracture profile specimen shows that crack propagates predominantly along bainitic plate or martensitic lath boundary (Fig. 5(a)), sometimes crosses them after hydrogen charging (Fig. 5(b)). On the fracture surface of hydrogen-charged tensile specimen, rhombic inclusions were observed, as shown in arrow A of Fig. 6(a). Energy spectrum analysis indicated that the rhombic inclusion was Ti(N,C) (Fig. 6(b)). In the figure, noticed that the small facet with brittle fracture was produced around the inclusion, which indicated that the interfacial decohesion of the matrix/inclusion interface leads the brittle fracture, and the Ti(N,C) inclusion was not observed on the fracture surface of hydrogen-uncharged specimens.

4. Discussion

Figure 3(b) shows that the \(E_{11}\) of specimen B is less than that of specimen C, which is related to microstructure. The bainite/martensite dual-phase microstructure obtained by thermomechanical heat-treatment is finer than that of conventional heat-treatment (Fig. 1). The finer the bainite/martensite dual-phase microstructure, the more the phase boundary is. Since the phase boundary is a hydrogen trap\(^{16}\), the increase of phase boundary also leads to increase of hydrogen traps, which makes hydrogen distributed homogeneously. At the same time, after thermomechanical heat-treatment, there is a large amount of defect produced by the process (such as high density dislocations and polygonized subgrain blocks) in the bainite/martensite dual-phase microstructure, which is also hydrogen traps. The hydrogen traps reduced diffusivity of hydrogen in steels and slowed down the segregation of hydrogen on the crack tip. Therefore, the fined microstructure obtained by thermomechanical heat-treatment improved obviously the resistance to HE. In addition, the amount of retained austenite obtained by thermomechanical heat-treatment is more than that of conventional heat-treatment. Since the retained austenite has good ductility, it may inhibit crack propagation; on the other hand, retained austenite also acts as a hydrogen trap\(^{17}\) which may reduce local hydrogen segregation, and prevent hydrogen from accumulating into crack tip. Hence, retained austenite improves the resistance to HE.

The result of observation on fracture profile specimens is consistent with Kikuta’s results\(^{18}\) as shown in Fig. 5. Since lath boundary is hydrogen trap, the accumulation of hydrogen in the interface results in reduction in the strength of interfaces. In addition, the fined bainite/martensite dual-phase microstructure makes crack constantly change direction, which consumes much more energy and leads to improvement of ductility.

In the steel, hydrogen is distributed heterogeneously. In local area, such as crack tip, microvoids, grain boundaries, inclusions, hydrogen concentration is very high. The reason is that when hydrogen migrates via diffusion and dislocation transport in steel, and encounters hydrogen trap, hydrogen is arrested, which leads to increase in hydrogen concentration of local area. When it exceeds critical value under certain stress conditions, crack can initiate there. Ti(N,C) is a strong irreversible hydrogen trap, moreover, the coarse Ti(N,C) inclusions (great than or equal to 1 \(\mu m\)) are easier to create hydrogen-induced cracking.\(^{19}\) The strong irreversible hydrogen trap results in the high segregated hydrogen concentration, and the low stress for crack initiation. In general, the uniformly and dispersedly distributed hydrogen trap may decrease the hydrogen diffusion rate and concentration in crack tip more effectively, by contrast, if the strong hydrogen trap is not distributed uniformly and dispersedly, the hydrogen could be segregated around it to higher concentration, which often imparts a high susceptibility.\(^{20}\) The rhombic Ti(N,C) inclusions were observed in hydrogen-charged tensile specimens, whose size is approximately 1.2 \(\mu m\) (Fig. 6(a)). According to decohesion theory, hydrogen lowers cohesion force of Ti(N,C) and matrix, thereby, stress to rupture is low, and the separation of Ti(N,C) and matrix is a brittle fracture with small facet, as shown in Fig. 6(a)).

5. Conclusions

(1) After thermomechanical heat-treatment, microstructure of steels is remarkably fined. The sizes of bainite and martensite change from average 10 to 5 \(\mu m\) in length and 0.7 to 0.6 \(\mu m\) in width by the conventional heat-treatment and thermomechanical heat-treatment.

(2) The susceptibility to hydrogen embrittlement increases as cathodic current density increases. The resis-
tance to hydrogen embrittlement of thermomechanical heat-treatment specimens is superior to that of conventional heat-treatment, which is related to refinement of micro-structure and increase of defects.

(3) Fracture profile specimen shows that crack predominantly propagates along bainite and martensite lath boundary, sometimes also crosses them after hydrogen charging.

(4) The rhombic Ti(N,C) inclusions are observed on the fracture of hydrogen-charged tensile specimens. The separation of Ti(N,C) and matrix is a brittle fracture with small facet.

REFERENCES

1) W. W. Gerberich and Y. T. Chen: Metall. Trans., 6A (1975), 271.
2) M. H. Peterson, B. F. Brown, R. L. Newbegin and R. E. Groover: Corrosion, 23 (1967), 142.
3) G. Sandoz: Metall. Trans., 3 (1972), 1169.
4) N. Bandyopadhyay, J. Kameda and C. J. McMahon, Jr.: Metall. Trans., 14A (1983), 881.
5) E. A. Steigerwald and W. D. Benjamin: Metall. Trans., 2 (1971), 606.
6) T. Boniszewski and F. Watkinson: Met. Mater., 7 (1973), No. 2, 90.
7) I. M. Bernstein and A. W. Thompson: Int. Met. Rev., 21 (1976), 269.
8) R. Kerr, F. Solana, I. M. Berstein and A. W. Thompson: Metall. Trans., 18A (1987), 1011.
9) E. Snape: Corrosion, 24 (1968), 261.
10) B. Pawlowski, A. Mazur and S. Gorczyca: Corros. Sci., 32 (1991), No. 7, 685.
11) J. Xu, X.-M. Dai and Y.-Z. Xia: Corrosion Metallurgy and Corrosion Resistant Metal Material, Zhe Jiang Science and Technique Publishing House, Zhe Jiang, (1981), 77.
12) A. W. Thompson and I. M. Bernstein: Advances in Corrosion Science and Technology, ed. by M. G. Fontana and R. W. Stachle, Vol. 7, Plenum, New York, (1980), 53.
13) W.-G. Huang and H.-S. Fang: J. Iron Steel Res., 9 (1997) No. 2, 31.
14) J.-M. Xiao: Metal Corrosion under Stress, Chemistry Industry Publishing House, Beijing, (1990), 372.
15) Y.-L. Du and W.-Z. Tan: Mater. Prot., 21 (1988), No. 3, 10.
16) W.-H. Gye and J.-Y. Lee: J. Mater. Sci., 18 (1983), 271.
17) J.-H. He, X.-Y. Tang and N.-P. Chen: Acta Metall. Sin., 25 (1989), No. 1, A42.
18) Y. Kikuta and T. Araki: Hydrogen Effects in Metals, ed. by I. M. Bernstein and A. Thompson, The Metallurgical Society of AIME, New York, (1981), 309.
19) H. Y. Liou, R. I. Shieh, F. I. Wei and S. C. Wang: Corrosion, 49 (1993), No. 5, 389.
20) B. G. Pound: Acta. Mater. 46 (1998), No. 16, 5733.