Materials Science & Engineering A 662 (2016) 528–536

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Influence of cold deformation and annealing on hydrogen embrittlement of cold hardening bainitic steel for high strength bolts

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ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form
21 March 2016
Accepted 23 March 2016
Available online 24 March 2016

Keywords:
Hydrogen embrittlement
Cold hardening bainitic steel
Cold deformation
Annealing
Hydrogen trapping
High strength bolt steel

ABSTRACT

The influence of cold drawing and annealing on hydrogen embrittlement (HE) of newly developed cold hardening bainitic steel was investigated by using slow strain rate testing (SSRT) and thermal desorption spectrometry (TDS), for ensuring safety performance of 10.9 class high strength bolts made of this kind of steel against HE under service environments. Hydrogen was introduced into the specimen by electrochemical charging. TDS analysis shows that the hydrogen-charged cold drawn specimen exhibits an additional low-temperature hydrogen desorption peak besides the original high-temperature desorption peak of the as-rolled specimen, causing remarkable increase of absorbed hydrogen content. It is found that cold drawing significantly enhances the susceptibility to HE, which is mainly attributed to remarkable increase of diffusible hydrogen absorption, the occurrence of strain-induced martensite as well as the increase of strength level. Annealing after cold deformation is an effective way to improve HE resistance and this improvement strongly depends on annealing temperature, i.e. HE susceptibility decreases slightly with increasing annealing temperature up to 200 °C and then decreases significantly with further increasing annealing temperature. This phenomenon is explained by the release of hydrogen, the recovery of cold worked microstructure and the decrease of strength with increasing annealing temperature.

1. Introduction

High strength bolts of 8.8 strength class and above have been widely used since 1930s mainly owing to their high strength level and accordingly high fastening efficiency for equal size, mass, and stiffness [1]. However, hydrogen embrittlement (HE), or in other words, hydrogen-induced delayed fracture (HIDF) has been one of the top issues in developing high strength bolts for it causes unexpected failure in service well below their design life [1–7]. The susceptibility to HE generally increases with enhancing steel strength levels, and therefore the strength level of high strength bolts had been limited to about 1000–1200 MPa [1,4].

The steels used for manufacturing high strength bolts are usually medium-carbon steels, alloy steels and boron steels. To meet the requirements of cold forming, spheroidizing annealing treatment of the wire material is often required before forming, and to meet the mechanical requirements quenching and tempering (QT) heat treatment is generally applied to after bolt making. Besides efforts to prevent HE, great attentions have also been paid to simplify the manufacturing process especially to eliminate the above mentioned heat treatment of high strength bolts, and thus to reduce their manufacturing costs [1]. Among these achievements, cold hardening bainitic steels for 10.9 strength class bolts have been successively developed [8–11]. This kind of steel wire generally comprises granular bainitic microstructure with as-rolled tensile strength level around 900 MPa. The steel wire also possesses enough ductility to be used directly to make bolts without spheroidizing treatment, and further strengthening could be obtained through suitable degree of cold drawing (usually in the cold reduction range of 20–40%). Besides cold drawing, the steel wire is also subjected to cold heading into the fastener shape and threading. Therefore, subsequent annealing treatment is usually conducted to stabilize the cold worked microstructure and to produce fasteners with satisfactory properties [8–10].

The strength level of 10.9 strength class bolts made of this kind of steel is over 1000 MPa, a risk to susceptibility to HE might still exist [5,11]. Moreover, plastic deformation introduced by cold working should be considered as a significant factor affecting HE [12–16], in addition to applied stress and hydrogen content, which

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http://dx.doi.org/10.1016/j.msea.2016.03.104
0921-5093/

are considered as the influencing factors for high strength bolts [1,4–7]. It is also known that hydrogen entry into steels increases with plastic strain [14–19]. However, there are few studies concerning the influence of annealing treatment after cold deformation on hydrogen trapping and HE behavior of cold hardening steels [19,20]. Therefore, in this study, the influences of cold drawing and subsequent annealing treatment on HE as well as hydrogen trapping behavior of newly developed cold hardening bainitic steel for 10.9 class high strength bolts were investigated. Understanding of such behavior is important for ensuring safety performance of high strength bolts made of this kind of steel against HE under service environments.

2. Material and experimental procedure

2.1. Materials and specimen preparation

The material used was a commercial low-carbon Mn-B-Ti type bainitic steel for the production of 10.9 class high strength bolts through cold hardening process. The chemical composition of the tested steel is listed in Table 1. The steel was supplied in the form of as-hot rolled 13 mm diameter wires. The 13 mm wires were experimental cold drawn, after chemical descaling and coating, to reach several wire sizes with different degrees of cold drawing reduction of area γ ($\gamma = 1\text{-}A_i/A_0$, where A_i is the area of any drawn wire, A_0 is the initial wire area before cold drawing) varying from 10% to 50%. After cold drawing, parts of the samples were annealed at temperatures in the range of 100–400 °C for 120 min.

Circumferentially notched round specimens, as shown in Fig.1 with notch root radius of 0.15 mm, were used for the slow strain rate testing (SSRT). The presence of a notch allows for obtaining a hydrostatic stress state in its proximity, thus, increasing the hydrogen mobility during loading and the embrittling effect of hydrogen. The stress concentration factor K_t of the notch was 3.2 [21]. Specimens for tensile testing are standard round bar with minimum diameter of 5 mm and gauge length of 25 mm. Specimens with diameter of 5 mm and length of 30 mm were used to study the hydrogen absorption and desorption behavior by using thermal desorption spectrometry (TDS). Hydrogen was introduced into specimens by electrochemical charging in a 0.1 mol/L NaOH aqueous solution at a current density of 2 mA/cm^2 for 72 h.

2.2. TDS and SSRT analysis

TDS was used for the analysis of hydrogen and the tests were carried out within 10 min after completing the hydrogen charging, unless otherwise indicated. The specimen was heated from ambient temperature to 800 °C at a constant heating rate of 100 °C/h, unless otherwise indicated. The hydrogen effusing out of the specimen was then analyzed by the quadrupolar mass spectrometer and the hydrogen content could be obtained through the integration of the hydrogen evolution curve.

SSRT tests were performed at room temperature using a WDML-300 kN type machine at a constant stroke speed of 0.005 mm/min corresponding to a nominal strain rate of 2.1×10^{-6}/s. At least three samples were tested and the results were the average of the three samples. After SSRT tests, the notch tensile stresses (σ_{NS0} and σ_{NS} for the uncharged and hydrogen-charged specimens, respectively) were obtained. The index of relative susceptibility to HE (HEI) of different specimens was determined by calculating the relative notch tensile strength loss, which is expressed as:

$$HEI(\%) = \frac{\sigma_{NS0} - \sigma_{NS}}{\sigma_{NS0}} \times 100\% \tag{1}$$

Table 1
Chemical compositions of the tested steel (wt%).

C	Si	Mn	P	S	Cr	Ti	B	Al
0.13	0.30	2.09	0.015	0.002	0.27	0.020	0.002	0.012

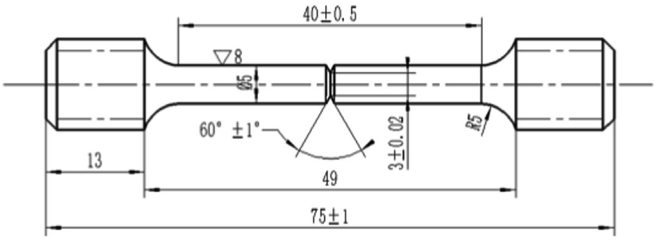

Fig. 1. Geometry and dimensions (in mm) of the notched specimen for SSRT with notch root radius of 0.15 mm and $K_t = 3.2$.

2.3. Microstructural and mechanical evaluation

Olympus GX51 optical microscope (OP) and ZEISS EVO.18 scanning electron microscope (SEM) were used for microstructural observation. The longitudinal section of specimen was etched in 3% nital solution after polishing. Rigaku 3014 type X-ray diffraction (XRD) instrument was used to determine the retained austenite (RA) volume fractions using a Co X-ray source operating at 35 kV and 40 mA. The specimens for transmission electron microscope (TEM) were sliced into 0.5 mm thick plate and subsequently ground down to a thickness of about 50 μm. These foils were finally electropolished in a twin-jet electropolishing apparatus using a standard chromium trioxide-acetic acid solution. Thin foils were examined in Hitachi H-800 TEM at an operating voltage of 200 kV. Tensile tests were conducted on a MTS 810 type universal testing machine with a constant cross-head speed of 1 mm/min at room temperature.

3. Results

3.1. Microstructures

Figs.2 and 3 show both OP and SEM microstructures of the tested steel wires at different conditions. For the as-rolled steel wire, it exhibits fine granular bainitic microstructure which consists of bainitic ferrites and martensite-austenite (M-A) islands (Figs. 2(a),(c) and 3(a) and (b)). Further XRD analysis reveals that the volume fraction of RA is about 7.7% (Fig.4). This kind of microstructure is mainly attributed to the low C content, rather high Mn content and the addition of microalloying elements of B and Ti, as well as the comparatively low finishing rolling temperature and fast cooling rate of the tested wires [1].

As cold drawing increases, bainitic ferrite laths were elongated and became slender and tended to align to the cold drawing direction (Fig. 2(b) and (d)). Owing to the strong plastic deformation undergone by the material, the dislocation density significantly increased and formed many tangled and cell-like dislocations, as shown in Fig. 3(c) and (d), which could significantly interfere and retard the movement of dislocations. Like that of transformation-induced plasticity (TRIP) steels, most of the RA transformed into martensite during the course of cold drawing (Figs. 2(d) and 4) [14,22]. This deformation-induced transformation leads to additional plasticity, which enables continuous drawing and strain strengthening. It is known that the size, shape and chemical composition of RA [23,24] as well as the partitioning of strain