JOURNAL OF IRON AND STEEL RESEARCH, INTERNATIONAL. 2014, 21(10): 951-955

Hydrogen Absorption and Desorption during Heat Treatment of AISI 4140 Steel

Ming-da ZHANG[1,2], Mao-qiu WANG[1], Han DONG[1]
(1. National Engineering Research Center of Advanced Steel Technology, Central Iron and Steel Research Institute, Beijing 100081, China; 2. School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China)

Abstract: Hydrogen plays an important role in the formation of quench cracks of structural steels. To clarify hydrogen absorption and desorption during heat treatment of AISI 4140 steel, thermal desorption spectrometry (TDS) analysis was carried out for the specimens in the as-rolled, as-quenched, and quenched and tempered conditions. Results show that hydrogen content increased from 0.127×10^{-6} in the as-rolled specimen to 0.316×10^{-6} in the as-oil-quenched specimen. After tempering at 200 ℃, the hydrogen content in the oil-quenched specimen decreased to 0.155×10^{-6}, and the peak temperature of hydrogen desorption increased from 200 to 360 ℃. From the dependence of hydrogen content in the as-quenched specimens on austenitizing time, it can be deduced that hydrogen absorption occurs during austenitizing. The simulation of hydrogen absorption contributes to a better understanding on the distribution of hydrogen during the heat treatment in structural steels.

Key words: steel; hydrogen absorption; heat treatment; thermal desorption spectrometry

Structural steels such as AISI 4140 with high strength and good toughness have been widely used after they are quenched and tempered. However, quench cracking, which is a fatal problem, may occur for these steels if the quenching process is not well controlled. It has been believed for a long time that residual stress caused by phase transformation and thermal stress is responsible for quench cracking of the as-quenched steel, which has extremely high strength and very low toughness. Recently, Lin and McMahon regarded quench cracking as hydrogen-emanated from the identical appearance of the fracture surfaces of quench cracking and hydrogen-induced cracking[1]. They found that quench cracking could be avoided by plating the steel with nickel, and concluded that hydrogen might be released by the breakdown of water molecules that contact the steel surface during quenching[1]. However, it has not been clarified whether the amount of hydrogen that might be absorbed during quenching is high enough to cause cracking. It might be too low to be accurately determined by the conventional analysis technologies for hydrogen measurement.

In recent years, thermal desorption spectrometry (TDS) analysis has been used to measure hydrogen content in steels with especially high accuracy[2,3]. For example, Akiyama et al.[4] carried out a lot of TDS analysis on hydrogen absorption of a similar steel JIS SCM435 during atmospheric exposure, the amount being as low as 10^{-9}. This work aims to investigate hydrogen absorption and desorption by TDS during heat treatment of AISI 4140 steel, which may suffer from quench cracking during water quenching. It also aims to understand whether the amount of hydrogen that might be absorbed during quenching is high enough to cause cracking.

1 Experimental

A commercial AISI 4140 steel with the chemical compositions shown in Table 1 was selected for the present study. Hot rolled bars of the steel of 12 mm in diameter were machined into specimens of 9 mm in diameter and 40 mm in length.

The specimens were heat treated before hydrogen

Foundation Item: Item Sponsored by National Basic Research Program (973 Program) of China (2010CB630800)

Biography: Ming-da ZHANG, Doctor Candidate; **E-mail**: zhangmd12@mails.tsinghua.edu.cn; **Received Date**: July 12, 2013

Table 1 Chemical compositions of the AISI 4140 steel investigated mass%

C	Si	Mn	P	S	Cr	Mo	Fe
0.41	0.18	0.75	0.015	0.007	1.01	0.18	Balance

measurement by TDS analysis. Some specimens were heated to 860 ℃ in an air furnace and austenitized at the temperature for a holding time in the range of 5－300 min, followed by oil quenching to room temperature. The as-oil-quenched specimens were surface polished to remove the oxide layer in 15 min and kept in liquid nitrogen to avoid hydrogen release before TDS analysis. All these specimens were analyzed by TDS in 1 week after heat treatment. It is generally believed that the hydrogen release in such a short period at liquid nitrogen temperature is very little. The measurement results of these samples which were performed in random sequence showed good regularity. This further proves that the scheme is reasonable and accuracy. The other specimens were also heated to 860 ℃ in an air furnace and austenitized at the temperature for 90 min, followed by oil quenching, water quenching and air cooling to room temperature respectively. One of the oil-quenched specimens was further tempered at 200 ℃ for 120 min. The as-quenched specimens, the quenched and tempered specimen, and one as-rolled specimen were also surface polished to remove the oxide layer for hydrogen content measurement by TDS in 24 h after heat treatment.

The thermal desorption spectrometry system used in this work was imported from Japan to analyze the mass of hydrogen contained in steel pieces. The high measurement accuracy of hydrogen concentration can reach 10^{-8}, making it one of the most effective equipments of hydrogen content analysis for steels at present. Before TDS analysis, the specimens were first ultrasonic cleaned for 5 min, and then put into the TDS machine. The time for preparing TDS analysis of all the specimens was kept around 30 min. The specimens were heated from room temperature to 800 ℃ in a vacuum furnace at the heating rate of 100 ℃/h, and hydrogen desorption rate was measured by Q-mass and recorded automatically. The recorded data were processed and converted into TDS curve and hydrogen content by the support software-Hydrogen Calculation Software. TDS curve showed the variation of hydrogen desorption rate with heating temperature, and the hydrogen content for the specimen measured was obtained by the amount of hydrogen desorption divided by the mass of the specimen.

2 Results and Discussion

2.1 Effect of quenchant on TDS curve and H content

Fig. 1 shows TDS curves of the AISI 4140 steel in different heat treatment conditions. For the as-rolled specimen, one hydrogen desorption peak at around 300 ℃ is found and the hydrogen content corresponding to this peak is 0.127×10^{-6}, as shown by H-peak in Table 2. Since the as-rolled specimen has been kept for a very long time before TDS analysis, hydrogen in the as-rolled specimen may not diffuse out by exposure at room temperature, and it is non-diffusible, which can also be seen from the relatively high peak temperature of hydrogen desorption at 300 ℃. It is believed that the non-diffusible hydrogen is not responsible for hydrogen-induced cracking[5]. Thus, the non-diffusible hydrogen in the as-rolled specimen does not have much relation with quench cracking.

Compared with the as-rolled specimen, the as-quenched specimens, no matter the quenchant is oil, water or air, show an additional hydrogen desorption peak at 200 ℃, as shown in Fig. 1. The hydrogen content corresponding to this low temperature peak is $0.213\times10^{-6}-0.300\times10^{-6}$, as shown by L-peak in Table 2. According to previous results, the hy-

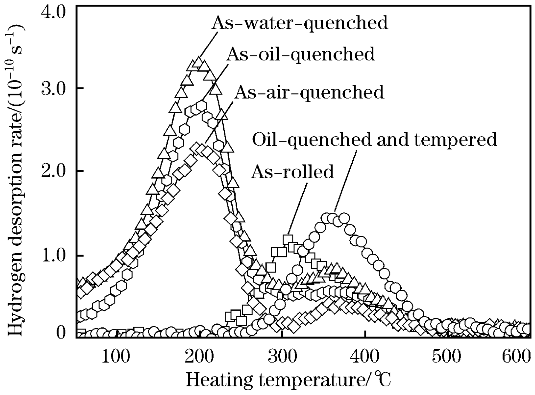

Fig. 1 TDS curves of specimens in as-rolled, as-quenched, and quenched and tempered conditions

Table 2 Hydrogen content in the specimens under different heat treatment conditions 10^{-6}

Specimen	L-peak H content	H-peak H content	Total H content
As-rolled	—	0.127	0.127
As-water-quenched	0.300	0.098	0.398
As-oil-quenched	0.243	0.073	0.316
As-air-quenched	0.213	0.060	0.273
Quenched and tempered	—	0.155	0.155

drogen corresponding to this peak may diffuse out and it is diffusible, which means this peak will disappear if the specimen is exposed at room temperature for a relatively long time[6]. This peak may also disappear if the as-quenched specimen is tempered at 200 ℃ for 120 min (Fig. 1). It is proved that diffusible hydrogen is responsible for hydrogen-induced cracking, and it may occur if the diffusible hydrogen content reaches a critical value, the so-called critical hydrogen content[6].

The hardness and strength for the as-quenched specimens of the AISI 4140 steel are very high, and the as-quenched specimens may have high susceptibility to hydrogen-induced cracking. The critical hydrogen content of hydrogen-induced delayed fracture for a similar steel JIS-SCM435 at the tensile strength of 1450 MPa was measured to be less than 0.10×10^{-6}[6]. Thus, the diffusible hydrogen content in the range of $0.213\times10^{-6}-0.300\times10^{-6}$ in the as-quenched specimens of the AISI 4140 steel seems to be high enough to cause hydrogen-induced cracking. It indicates that hydrogen may play an important role in the formation of quench cracking during quenching, as proposed by Lin and McMahon[1].

From Table 2, it can also be seen that the hydrogen content of the as-quenched specimens is also dependent on the quenchant. The as-quenched specimen for the oil quenchant has the hydrogen content higher than that for the air quenchant and lower than that for the water quenchant. This difference can be explained by Lin and McMahon, in which it is regarded that hydrogen might be released by the breakdown of water molecules that contact the steel surface during quenching[1]. However, it is unlikely that all the hydrogen corresponding to the low temperature peak of the as-quenched specimens is introduced from the quenchant during quenching, since the as-quenched specimen for the air quenchant is also high. Hydrogen absorption may also occur before quenching the steel.

2. 2 Effect of austenitizing time on TDS curve and H content

Fig. 2 shows some TDS curves of the as-quenched specimens after austenitized at 860 ℃ for different time and quenched into oil. It is apparent that the low temperature peak for hydrogen desorption at around 200 ℃ varies with austenitizing time, indicating that hydrogen absorption depends on austenitizing time.

Fig. 3 shows the variation of hydrogen content (L-peak) in the as-quenched specimens with austenitizing time. Despite the two points for the long austenitizing time, the other points show an increasing tendency of the hydrogen content with austenitizing time. This indicates that the hydrogen is mainly absorbed during austenitizing instead of during quenching, which was proposed by Lin and McMahon[1]. The hydrogen substances in the furnace or on the surface of specimens are most likely to become the major source of hydrogen and hydrogen absorption may occur continuously during austenitizing until a saturation state is reached. The last two points in Fig. 3 show the hydrogen concentration decreased slightly. It is presumably due to the reduction of hydrogen traps such as dislocations and grain boundaries, which might decrease with increasing austenitizing time and reducing the solubility of hydrogen in steel.

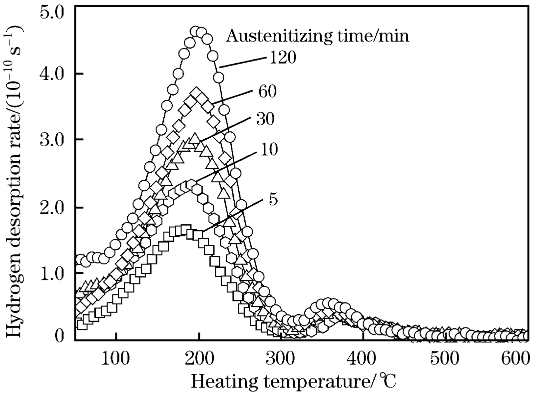

Fig. 2 TDS curves of the as-oil-quenched specimens after austenitizing at 860 ℃ for different time

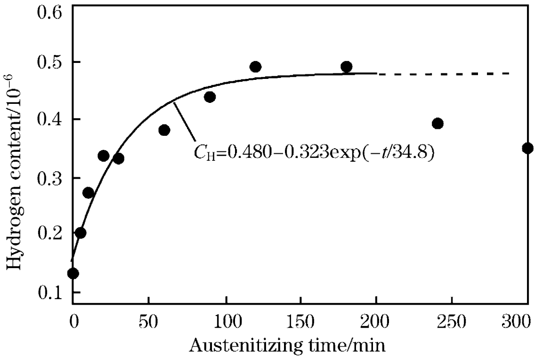

Fig. 3 Variation of hydrogen content in as-oil-quenched specimens with austenitizing time

The variation of hydrogen content with austenitizing time can be described by an exponent equation, as shown in Fig. 3. According to Fick's second law of diffusion in a long cylinder[7], the apparent hydrogen diffusion coefficient in the AISI 4140 steel at the austenitizing temperature of 860 ℃ can be calculated to be about 1.75×10^{-9} m^2/s, which is two orders higher than that in a similar steel JIS-SCM 435 at room temperature[8]. The ferritic body centred cubic (bcc) or body centred tetragonal (bct) structure has a higher hydrogen diffusion rate and a lower solubility than the austenitic face centred cubic (fcc) structure at the same temperature[9]. But in this study, the temperature factor can make the hydrogen diffuse faster in austenite at high temperature than in martensite at room temperature.

$$C_{\mathrm{H}} = C_{\infty} + 0.72(C_0 - C_{\infty})\exp(-22.2Dt/d^2) \tag{1}$$

where, C_{H} is the real time hydrogen concentration; C_0 is the initial hydrogen concentration; C_{∞} is the saturated hydrogen concentration; D is the hydrogen diffusion coefficient; t is the austenitizing time; and d is the diameter of cylindrical specimen.

According to the fitting equation, the hydrogen absorption reaches a saturation value of about 0.48×10^{-6} when the austenitizing time is long enough. The hydrogen content is high enough for hydrogen-induced cracking of the as-quenched specimens of the AISI 4140 steel. The introduction of high concentration hydrogen should cause much more attention.

2.3 Hydrogen distribution with austenitizing time

The actual distribution of hydrogen in steel is very complex which often depends on hydrogen traps[10]. According to the TDS results for the AISI 4140 steel, the absorption of hydrogen might occur mainly during austenitizing. Using the hydrogen diffusion coefficient of 1.75×10^{-9} m^2/s obtained for the AISI 4140 steel at the austenitizing temperature of 860 ℃, the variation and distribution of hydrogen concentration with austenitizing time are simulated by the finite difference method. The results describe the process of hydrogen entry into the steel during the heat treatment, which can help us better understand the distribution of hydrogen. Long cylindrical specimen can also be simplified into one-dimensional model along the radial direction[6].

Figs. 4 and 5 show the variation of relative hydrogen concentration in the hydrogen diffusion model with austenitizing time and the variation of relative hydrogen concentration in the hydrogen diffusion model with different radius position in cylindrical sample. The radius of the sample, R, starts from the central axis of the cylindrical sample and ends at the surface. C_i/C_0, which is called the relative hydrogen concentration, equals the internal hydrogen concentration of the sample divided by the hydrogen concentration of the sample surface which is regarded as a constant for environmental hydrogen concentration.

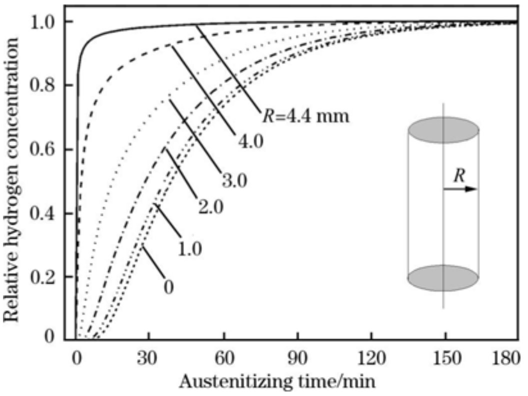

Fig. 4 Variation of relative hydrogen concentration with austenitizing time obtained by numerical calculation

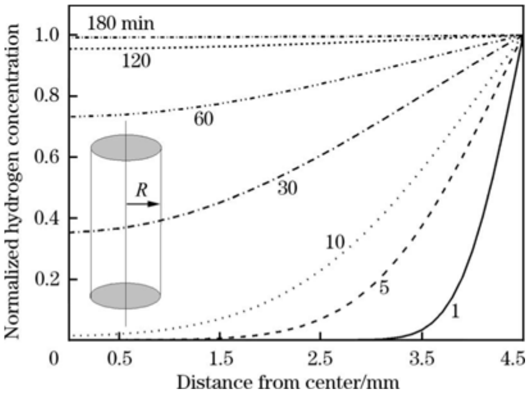

Fig. 5 Distribution of relative hydrogen concentration along radial direction of the cylindrical sample obtained by numerical calculation

Fig. 4 shows that the relative hydrogen concentration of the sample surface (R=4.5 mm) grows very fast and approximates to 1 in a short period of time due to the high hydrogen diffusion capacity at high temperature. At the same time, the internal hydrogen concentration of the sample also grows very fast. The internal hydrogen concentration in the center of the cylindrical specimen (R=0 mm) reaches 90% of C_0 after austenitizing for 90 min. The simulation results and experimental results can be well matched.

Fig. 5 shows the distribution of relative hydrogen concentration along the radial direction with austenitizing time. It can be seen that hydrogen distribution is steep at the austenitizing time of 30 min. With increasing austenitizing time, the hydrogen distribution is becoming flatter. The relative hydrogen concentration at the center of the specimen reaches over 70% of the saturated hydrogen content at the austenitizing time of 60 min. The hydrogen content of the sample is almost saturated when the austenitizing time exceeds 120 min.

From the above results, it can be concluded that hydrogen absorption during austenitizing should be carefully controlled to avoid quench cracking of the AISI 4140 steel. Actually, avoidance of quench cracking by plating the steel with nickel, which was proposed by Lin and McMahon[1], might also effectively hinder hydrogen entry into the steel during austenitizing as well as during quenching.

3 Conclusion

Hydrogen absorption and desorption during heat treatment of AISI 4140 steel have been investigated by means of TDS analysis. It can be concluded that hydrogen absorption occurs mainly during austenitizing in the air furnace, and the hydrogen content absorbed can reach 0.48×10^{-6}, which is high enough for hydrogen-induced crack. To avoid quench cracking of the AISI 4140 steel, hydrogen absorption during austenitizing should be carefully controlled.

References:

[1] X. Y. Liu, C. J. McMahon Jr. , Mater. Sci. Eng. A 499 (2009) 540-541.

[2] M. Q. Wang, E. Akiyama, K. Tsuzaki, Scripta Mater. 52 (2005) 403-408.

[3] M. Nagumo, Mater. Sci. Technol. 20 (2004) 940-950.

[4] E. Akiyama, K. Matsukado, M. Q. Wang, K. Tsuzaki, Corros. Sci. 52 (2010) 2758-2765.

[5] K. Takai, R. Watanuki, ISIJ Int. 43 (2003) 520-526.

[6] M. Q. Wang, E. Akiyama, K. Tsuzaki, Corros. Sci. 48 (2006) 2189-2202.

[7] C. J. Carneiro Filho, M. B. Mansur, P. J. Modenesi, B. M. Gonzalez, Mater. Sci. Eng. A 527 (2010) 4947-4952.

[8] M. Q. Wang, E. Akiyama, K. Tsuzaki, Mater. Sci. Eng. A 398 (2005) 37-46.

[9] V. Olden, C. Thaulow, R. Johnsen, Mater. Des. 29 (2008) 1934-1948.

[10] M. Dadfarnia, P. Sofronis, T. Neeraj, Int. J. Hydrogen Energ. 36 (2011) 10141-10148.