Microstructure characteristic of hot formed 22MnB5 steel and its relationship with delayed hydride cracking property

Hua Wang\textsuperscript{1a*}, Shiyu Hao\textsuperscript{1b}, Baolei Wang\textsuperscript{1c}, Chunfu Kuang\textsuperscript{2d}

\textsuperscript{1}Instrumental Analysis Center, Shanghai University, 200444, China
\textsuperscript{2}PanGang Group Xi Chang Steel and Vanadium Co., Ltd, Si Chuan, 615000, China
\textsuperscript{1a*}wh225@shu.edu.cn, \textsuperscript{1b}shiyuao@shu.edu.cn, \textsuperscript{1c}wangbaolei@shu.edu.cn, \textsuperscript{2d}kuangchunfu@126.com

Abstract—Hydrogen-induced delayed cracking is an important factor leading to the failure of ultra-high strength steels during service, thus in this study, the mechanical properties and hydrogen trapping of hot formed 22MnB5 steel considering different content of V (0, 0.05, 0.09 wt.%) and corresponding microstructure were investigated. Slow strain rate tensile tests (SSRT) were applied to obtain the tensile strength and elongation of samples under different medium conditions (air, HCl immersion and electrolytic hydrogen charging). Besides, microstructure and atomic distribution morphology of the samples were detected and analyzed by transmission electron microscope (TEM) and atomic probe tomography (APT) technique. Results showed that both resistances of hydrogen-induced delayed cracking in MnB-V\textsubscript{0} and MnB-V\textsubscript{9} samples were obviously better than that in MnB-V\textsubscript{0} sample, besides, the delayed cracking resistances of MnB-V\textsubscript{9} and MnB-V\textsubscript{5} samples did not improve with the increase of V content, but basically remained the same. Lamellar residual austenite was found in all samples, but no hydrogen was grasped in the same area according to APT result. There was intragranular cementite in all samples, and it has grasped H in the same position. The carbides formed by V, Ti and other alloying elements were found in MnB-V\textsubscript{5} and MnB-V\textsubscript{9} and were considered to be an important factor in improving the anti-hydrogen delayed cracking performance of the steel.

1. Introduction
Hot-formed steel is an important kind of steel commonly used in manufacturing automobile structural parts. Hot stamping process, which combines the forming and quenching process of parts, can effectively solve the cracking and spring-back problems of parts under conventional stamping process, and is an important method to improve vehicle safety at present. However, the hydrogen-induced delayed cracking behavior of ultra-high strength steel plate becomes a more severe phenomenon that influences the application and service of steel. Therefore, with the wider application of ultra-high strength steel in automobile field, it is more necessary to study the delayed cracking behavior of ultra-high strength steel \cite{1}.

Hydrogen is reported to diffuse and penetrate in the steel substrate during both production and application processes, and the hydrogen adsorbed in micro cracks and cavities on metal surfaces reduce their surface energy and facilitated crack nucleation and extension. Studies showed that there were many factors, such as elements, precipitates, defects in substrates and steel microstructure that could influence the hydrogen embrittlement resistance in high strength steel \cite{2}. Li et al \cite{3} reported that adding appropriate amount of micro alloying element in steel is an effective way in improving the hydrogen embrittlement resistance of steel. V, as a common metal element among all the microalloying elements in industry, not
only can improve the mechanical properties of steels, but also can improve the hydrogen embrittlement resistance of high strength steels.

In the present work, the mechanical properties and hydrogen-induced delayed cracking behavior of hot-formed 22MnB5 ultra-high strength steels containing different V contents with various hydrogen charging methods of air, HCl immersion and electrolytic H₂SO₄ were studied. The hydrogen-induced delayed cracking behavior mechanism was analyzed with employment of microanalysis technique of scanning electron microscope (SEM) and TEM. The study is expected to provide reference for the hydrogen-induced delayed cracking research in high strength steel plate.

2. Experimental Procedure

Three groups of 22MnB5 steel plates were provided from a domestic steel company, and the chemical compositions were listed in Table 1. The quenching processes of the steel plate are as follows: heating to temperature of 900-930 °C and holding for 3-5 min, then quenching to 800-850 °C, holding for 5-10 s, finally cooling to room temperature at a rate about 30 °C/s. The annealing process is as follows: heating to 720 °C at a rate of 5 °C/s and holding for 120 s, then rapidly cooling to 280 °C at a rate of 40 °C/s, over aging for 600 s, finally cooling to room temperature.

| Chemical compositions (wt.%) of 22MnB5 steels | C  | Si  | Mn  | P  | S  | Cr  | Ti  | B  | V  |
|---------------------------------------------|----|-----|-----|----|----|-----|-----|----|----|
| MnB-V0                                      | 0.220 | 0.26 | 1.28 | 0.008 | 0.002 | 0.16 | 0.025 | 0.0029 | 0 |
| MnB-V5                                      | 0.240 | 0.25 | 1.30 | 0.008 | 0.002 | 0.16 | 0.027 | 0.0029 | 0.052 |
| MnB-V9                                      | 0.236 | 0.24 | 1.30 | 0.007 | 0.002 | 0.15 | 0.025 | 0.0027 | 0.09 |

The plate with a thickness of 1.2 mm was cut to a standard tensile sample as shown in Fig. 1. During experiment, low strain rate combined with three different hydrogen charging methods (air, HCl immersion and electrolytic H₂SO₄) were employed to simulate the various states of delayed cracking reaction. The first group of samples were tested in air; the second group was stretched in HCl solution at 0.1 mol/L; the third group was electrolytically charged with hydrogen and stretched in electrolyte (H₂SO₄ solution at 0.5 mol/L with 500 mg/L thiourea). The current density was 1 mA/cm². Strain rates of the three groups were same to be 10⁻⁶ s⁻¹.

The phase analysis of samples was carried out using SMART APEXII X-ray diffractometer. The phase was irradiated by CuKα (λ=0.1548). The working voltage was 50kV and the scanning speed was 2°/min. The microstructure and fracture morphology of the samples were observed by JSM-6700F emission scanning electron microscope (F-SEM). The microstructures of samples were observed and studied more deeply by JEM-2100F field emission transmission electron microscope (FE-TEM).

LEAP4000 atomic probe tomography (APT) equipment was used to detect the element distribution of steels with various compositions under different treatment conditions. First, the samples were cut into rod-shaped needles of 0.5 mm × 0.5 mm × 20 mm dimensions, and then the needle-like samples were electrolytically polished with 2 % perchloric acid 2-Butoxy ethanol. During detecting, samples were cooled to 50K, the pulse voltage frequency was 5kHz and the pulse fraction was 20 %. The obtained data was analyzed and processed using PoSAP software.

Hydrogen concentrations in samples were detected by hydrogen thermal analyzer, which is composed of a four-stage mass spectrometer, a heating device and a recording device controlled by computer, and the result date were processed by a professional software attached to the system. During test, the heating rate was 100 °C/h and the holding temperature was 800 °C.
3. Results and Discussion

The microstructure and morphology of the samples are shown in Fig. 2, which shows that the microstructures of 22MnB5 hot formed steel are fine martensite and fine carbides distributed around the martensite. It is known that the microstructure of hot formed steel is mainly composed of martensite with high dislocation density and a small amount of residual austenite. The property of hydrogen-induced delayed cracking is related to dislocation density, precipitation of the second phase and morphology and distribution of residual austenite. Besides, during the hot stamping process, the matrix of the material undergoes phase transformation and lattice distortion, which induces many defects and internal stresses and is highly susceptible to hydrogen-induced delayed cracking in this kind of steel.

Fig. 2 Metallographic morphology of 22MnB5 steels after annealing; (a) MnB-V0, (b) MnB-V0, (c) MnB-V9

The stress-strain curves of the three samples after SSRT test under three different conditions were shown in Fig. 3. The corresponding data were listed in Table 2. It can be found that there are elastic deformation, uniform plastic deformation and non-uniform plastic deformation, but no obvious yield stage in the stress-strain curves. Besides, compared Fig. 3a with b, it was obviously that the tensile strength and elongation of the samples decreased when the samples were in hydrogen environment, and the elongation was even only 1/3 to 1/6 of that in air environment. Thus, hydrogen can seriously influence the mechanical property of 22MnB5 steel especially when at a high concentration. As is known, the reason is that in the process of dynamic tension, when the plastic deformation occurs, the dislocation in the specimen multiply and move greatly, and the hydrogen atoms were carried by the dislocation to spread and gather in the three-dimensional stress zone. At the same time, the hydrogen atom reduced the bonding force between the matrix atoms, resulting in the sample even when it was subjected to lower external force.

Fig. 3 Simultaneous tensile stress-strain curves of the three samples in different environments of (a) air, (b) HCl solution immersion and (c) H2SO4 solution electrolytic hydrogen charging
Table 2 Mechanical properties of the samples tested by SSRT under different medium conditions

| Steels  | Test conditions       | TS/MPa | EL/% |
|---------|-----------------------|--------|------|
| MnB-V0  | Air                   | 1785   | 11.9 |
|         | HCl immersion         | 620    | 1.9  |
|         | Electrolytic hydrogen charging | 240 | 0.5  |
| MnB-V5  | Air                   | 1750   | 12.8 |
|         | HCl immersion         | 1215   | 3.9  |
|         | Electrolytic hydrogen charging | 270 | 0.9  |
| MnB-V9  | HCl immersion         | 1065   | 3    |
|         | Electrolytic hydrogen charging | 300 | 0.9  |

Moreover, Fig. 3b and c showed the tensile elongation and strength of MnB-V0 samples under hydrogen atmosphere were obviously lower than MnB-V5 and MnB-V9 samples, that is, V addition in 22MnB5 steel is workable in improving resistance property of hydrogen embrittlement. But the mechanical property of the steel does not increase with the V content addition, on the contrary, the tensile strength of sample with 0.09 wt.% V showed serious decrease compared with the sample with 0.05 wt.% V in both air and HCl solution immersion conditions.

The residual hydrogen contents in the samples after tensile test were listed in Table 3. It shows that except for the electrolytic hydrogen charging samples, the hydrogen content in the other two groups of samples are at low levels. Combined with the changes of the mechanical properties shown in Table 2, we found that when a small amount of hydrogen is introduced into the sample, the performance of the sample decreases to a certain extent, but when the hydrogen reaches the order of magnitude of 1ppm, the performance of the sample will be seriously damaged, and it is no longer suitable for industrial applications.

Table 3 Hydrogen content test results in the sample after tensile test.

| Hydrogen charging method | Steels  | Hydrogen content (ppm) |
|--------------------------|---------|------------------------|
| Air                      | MnB-V0  | 0.003                  |
|                          | MnB-V5  | 0.002                  |
|                          | MnB-V9  | 0.003                  |
| HCl immersion            | MnB-V0  | 0.04                   |
|                          | MnB-V5  | 0.026                  |
|                          | MnB-V9  | 0.031                  |
| Electrolytic hydrogen charging | MnB-V0 | 3.62                   |
|                          | MnB-V5  | 1.62                   |
|                          | MnB-V9  | 1.79                   |

The fracture of SSRT of MnB-V5 in air (Fig. 4) that has many dimples on the fracture surface shows typical ductile fracture.

Fig. 5 shows the tensile fracture morphology of MnB-V5 immersed in HCl. Compared with the fracture surface of the air-stretched specimen, the tensile fracture dimple becomes larger after soaking in HCl, accompanied by obvious corrosion pits and microcrack areas, which means the plasticity of the specimen in this state decreases severely and tends to change to the cleavage fracture morphology gradually.

Fig. 6 shows the fracture morphology of MnB-V5 after electrolytic hydrogen-charged tensile. The ductile fracture characteristics of the specimens in this state almost disappear.
As reported in [4], a large amount of H generated by the cathodic reaction will be adsorbed on the surface of the sample, then the H atom will diffuse into the sample and enrich at the crack tip. The aggregated hydrogen atoms will reduce the binding force of the Fe-Fe bond and will further cause hydrogen embrittlement at the microscopic level. When the sample is loaded, the crack tip will become microcrack nucleation. Once the micro crack was formed, the hydrogen atom accelerates the crack growth by promoting the anodic dissolution of the crack tip or reducing the surface energy of the newly formed crystal plane.

Fig. 7 shows the XRD spectrum of MnB-V0, MnB-V5 and MnB-V9 sample. There is no or very low residual austenite, but only martensite in the samples.
Figs. 8, 9 and 10 are TEM results of MnB-V0, MnB-V5 and MnB-V9 stretched in air, HCl immersion and electrolytic hydrogen charging, respectively. The lath size of air tensile sample in Fig. 8a is finer than hydrogen charged samples in Fig. 8b and c, which is in line with the tensile test results that the former sample has more deformation than the latter ones.

Fig. 8d shows the micro structure of MnB-V0. A thin film between the two lath interfaces at the red circle in Fig. 8d and e indicate that a fine residual austenite lamellar was remained between martensite lath after annealing. Studies have shown that residual austenite can be used as a hydrogen trap to improve the delayed cracking resistance of materials. Fan et al.\(^5\) proposed that stable residual austenite is beneficial to improve hydrogen-induced delayed cracking, on the contrary, unstable residual austenite will aggravate the occurrence of hydrogen-induced delayed cracking.

Some intragranular phase were found precipitated in the martensite lath (Fig. 8f), and the SAD result proves them to be cementite. Cementite is formed in the process of slow phase transition, so its micro strain is small, and the resistance to hydrogen diffusion is weak. Generally, precipitation cementite on grain boundaries, especially thin film cementite will make delayed cracking sensitivity significantly enhanced.\(^6\) From the tensile test data of the other two groups of samples, results can be obtained that the addition of V suppresses the formation of grain boundary cementite and affects the delayed cracking resistance of the three groups of samples.

Fig. 8 TEM diagram of MnB-V0 sample microstructure after (a) air tensile, (b) HCl immersion tensile, (c) electrolytic hydrogen charging, and (d) martensite morphology, (e) martensite lath high resolution image, (f) cementite phase, (g) diffraction spot of f

---

\(^{5}\) Fan et al.

\(^{6}\) From the tensile test data of the other two groups of samples, results can be obtained that the addition of V suppresses the formation of grain boundary cementite and affects the delayed cracking resistance of the three groups of samples.
Comparing Fig. 8, with 9 and 10, we found the lath of MnB-V0 is thicker than MnB-V5 and MnB-V9 because of the lower deformation. Similar residual austenite lamellar was found in MnB-V5 (Fig.9a) and MnB-V9 (Fig.10a). Thinner cementite was found in MnB-V5 (Fig.9i). In addition, dispersed precipitation of second phase particles was found in MnB-V5 and MnB-V9 (red circle zone in Fig. 9 and 10), and the structure of them were identified to be V$_2$C by calibration result of selected area diffraction spot.

Fig. 11 shows the scanning energy spectrum analysis of the selected area in MnB-V0 sample. The enrichment of Fe, Mn and Cr on the martensite lath boundary were proved to be in a same field, which confirms the existence of residual austenite lamellar.
Fig. 12 shows the EDS result of MnB-V5 sample during TEM analysis. V and Ti elements were found to segregate in the precipitated particle area, which indicates the particle to be (VTi)C.

Some researchers [7] have studied that coherent TiC precipitates can capture hydrogen when the cathode is charged at room temperature, while incoherent TiC particles in steel cannot capture hydrogen at room temperature. Besides, the coherent and semi-coherent TiC particles capture hydrogen at the precipitate/ferrite interface. However, some researchers [8] have reported that hydrogen is trapped inside the VC particles rather than at the interface of the precipitate matrix. Chen [9] found that deuterium is mainly precipitated at the interface. Combining the research results of previous scholars, with the microstructure characteristics of 22MnB5 steel in this study, we considered that different types, contents, and sizes of carbides in each sample have captured hydrogen as hydrogen traps.
Fig. 13 and 14 are the element distribution diagrams of 22MnB5 samples measured by APT. The characteristics of the region shown in Fig. 13 are consistent with the TEM results in Fig. 8, that is, the lamellar residual austenite structure do exists in 22MnB5 steels, and its thickness is less than 5 nm. As we known, H has high solubility in austenite and is not easy to diffuse, for example, Park et al.\textsuperscript{[10]} have proposed that residual austenite is an interphase hydrogen trap with high binding energy. However, unlike the reported theory above, the enrichment of H element does not occur in the lamellar residual austenite field in the present work (Fig. 13a). MnB-V9 sample has a character of cementite precipitation as shown in Fig. 14, and this is also consistent with the TEM results of MnB-V5 steel in Fig. 9f. Through the elements distribution results, we found that there was an obvious enrichment of H in the carbides position, accompanied by the accumulation of C and Ti elements.

The H segregation in cementite, can be used as a hydrogen trap, for example, Nagao et al.\textsuperscript{[11]} found that the (Ti, Mo) C precipitates in martensitic steel can effectively capture the free hydrogen atoms in the steel. Gutierrez et al.\textsuperscript{[12]} have proposed that the intergranular fracture started at the deformation twins formed on the coarse cementite at the grain boundary and the local shear stress concentration at the cementite interface. Still more, Dong \textsuperscript{[13]} has found that the hydrogen diffusion rate of continuous annealing steel is obviously lower than that of batch annealing steel, and the reason is that many dispersed cementite particles in the ferrite grains of continuous annealing steel act as hydrogen traps, which restricts the diffusion of hydrogen atoms. It is generally believed that the fine and dispersed carbide in the grain but not the grain boundary will act as a hydrogen trap to slow down the diffusion of hydrogen in the material and to improve the delayed cracking resistance of the material. Unfortunately that no V was found in APT result, which was because the amount of V was low and the precipitates were dispersed.

According to all the tested results, the lamellar residual austenite in the three groups of samples didn’t grasp hydrogen. There was cementite in all the three groups of samples though the sizes were different, and they can grasp hydrogen around them. Since the above two characters in 22MnB5 steel were similar in all the three groups of samples, they were considered to has no important effect on the hydrogen delayed cracking resistance in the steel. However, in MnB-V5 and MnB-V9 samples, the intragranular vanadium carbide was found, which was considered to be a hydrogen trap and has improved the hydrogen delayed cracking resistance obviously.

4. Conclusion
Based on the results and discussions presented above, the conclusions are obtained as below:

(1) The hydrogen-induced delayed cracking resistance of the samples containing V is obviously better than the samples without V. Comparing with the samples of MnB-V5 and MnB-V9, the hydrogen-induced delayed cracking resistance dose not improve with the increase of V content, but remains at a same level.

(2) There was lamellar residual austenite found in 22MnB5 steels with or without V addition, but no hydrogen was grasped in the same area according to APT result.

(3) There was intragranular cementite in all samples, and it has grasped H in the same position.

(4) Intragranular vanadium carbide was found in MnB-V5 and MnB-V9 samples, which was considered to be the hydrogen trap and was a key factor in improving the hydrogen delayed cracking resistance.

References
[1] Gianfranco Lovicu et al. Hydrogen Embrittlement of Automotive Advanced High-Strength Steels[J]. Metallurgical and Materials Transactions A, 2012, 43(11): 4075-4087.
[2] Chen Y S, Lu H Z, Liang J T, et al. Observation of hydrogen trapping at dislocations, grain boundaries, and precipitates. [J]. Science (New York, N.Y.),2020,367(6474): 171-175.
[3] Li J.X, Wang Y.B, Chu W.Y, et al. Effect of alloying element vanadium on hydrogen embrittlement sensitivity for rail steel[J]. Journal of Chinese Society for Corrosion and Protection, 1998(02): 35-40.
[4] Verpoort C, Duquette D J, Stoloff N S, et al. The influence of plastic deformation on the hydrogen embrittlement of nickel[J]. Material Science & Engineering, 1984, 64(1): 135-145.

[5] Fan Y H, Zhang B, Yi H L, et al. The role of reversed austenite in hydrogen embrittlement fracture of S41500 martensitic stainless steel[J]. Acta Materialia, 2017, 139: 188-195.

[6] Hong S, Lee J, Lee B J, et al. Effects of intergranular carbide precipitation on delayed fracture behavior in three Twinning Induced Plasticity (TWIP) steels[J]. Materials Science & Engineering A, 2013, 587: 85-99.

[7] Depover T, Verbeke K. The effect of TiC on the hydrogen induced ductility loss and trapping behavior of Fe-C-Ti alloys[J]. Corrosion Science, 2016, 112(11): 308-326.

[8] Wang Y, Hu S, Li Y, et al. Improved hydrogen embrittlement resistance after quenching–tempering treatment for a Cr-Mo-V high strength steel[J]. International Journal of Hydrogen Energy, 2019, 44(54): 1-10.

[9] Chen Y S, Haley D, Gerstl S S A, et al. Direct observation of individual hydrogen atoms at trapping sites in a ferritic steel[J]. Science, 2017, 355(6330): 1196-1199.

[10] Park Y D, Maroef I S, Olson D L. Residual austenite as a hydrogen trap in steel welds[J]. Welding Journal, 2002, 81(2): 27S-35S.

[11] Nagao A, Smith C D, Dadfarnia M, et al. The role of hydrogen in hydrogen embrittlement fracture of lath martensitic steel[J]. Acta Materialia, 2012, 60(13-14): 5182-5189.

[12] Gutierrez U, Raabe D, et al. Influence of Al content and precipitation state on the mechanical behavior of austenitic high-Mn low-density steel[J]. Scripta Materialia, 2013: 343-347.

[13] Dong F B, Du L X, Liu X H, et al. Effect of annealing method on Microstructure and properties of boron bearing cold rolled deep drawing enamel steel[J]. Journal of Northeast University Natural Science Edition, 2013, 34(10): 1412-1415.