Experimental investigation on the hydrogen embrittlement characteristics and mechanism of natural gas-hydrogen transportation pipeline steels

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Abstract
Hydrogen blended with natural gas is one of the best ways for large-scale hydrogen transportation; however, pipeline steels exploited for transferring natural gas have the risk of hydrogen embrittlement. Therefore, the hydrogen damage mechanism and resistance property of different steel pipelines should be carefully examined to select suitable materials for the task mentioned above. The common X42, X52, X70, and AISI 1020 are taken into account as research objects. Their mechanical properties and hydrogen absorption properties in a hydrogen environment are investigated to explore further factors affecting the hydrogen embrittlement of material. Dynamic slow strain rate tensile test results show that these materials exhibit varying hydrogen embrittlement sensitivity in a hydrogen environment. AISI 1020 has the highest hydrogen embrittlement susceptibility, then X70, and X42 presents the lowest one. Generally, hydrogen embrittlement behaviours are strengthened by increasing the current density. As the current density grows, the fracture mode of pipeline steels transforms from the ductile fracture to the quasi-cleavage fracture and finally turns into the cleavage fracture. The hydrogen embrittlement fracture of the tensile specimen results from the action of the HEDE and HELP in various zones. TDS test results indicates that the content of C and Mn significantly influence on the hydrogen solubility in metal materials.

1. Introduction
Hydrogen has the advantages of high combustion value and no pollution, making it an excellent energy carrier for energy regeneration [1]; nevertheless, hydrogen is difficult to store, and it is flammable and explosive. Therefore, how to realize large-scale safe hydrogen transportation has become an urgent problem to be solved. Some scholars have proposed that hydrogen-compressed natural gas (HCNG) can be directly transported by blending hydrogen into existing natural gas pipelines. The method saves cost and has the immediate benefit in decreasing the amount of CO₂ produced by burning the gas mixture. So, it is currently considered the best way to achieve large-scale hydrogen transportation [2]. Besides, it is also an effective way to solve the problem of large-scale wind power and solar power consumption. Current research show that, the volume fraction of hydrogen in HCNG transportation pipelines is usually controlled within 20% around the world, and the corresponding operating pressure of the transportation pipelines is lower than 5.38 MPa. For most of the in-serviced HCNG transportation pipelines, the volume fraction of hydrogen is less than 10%, and the operating pressure is lower than 7.7 MPa. The reason why there are strict requirements on the hydrogen volume fraction and the pipeline operating pressure in the HCNG transportation pipeline is that the presence of hydrogen may increase the risk of premature failure of natural gas pipelines from hydrogen damage. In the hydrogen-containing environment, mechanical properties of steel, such as ductility and toughness, would gradually deteriorate, even leading to the sudden failure of materials [3, 4].
Pipeline steels for long-distance transportation of natural gas require the use of low-alloy high-strength steel with high strength, high toughness, excellent workability, and weldability. It is generally believed that the higher the strength of steel, the greater the possibility of hydrogen embrittlement [5]. Due to its excellent mechanical properties, steels such as X70, X42 and X52 are widely used in long-distance natural gas pipelines. Among them, X70 advanced pipelines steel are commonly exploited in China and Australia as long-distance natural gas pipelines [6], and AISI 1020 steel is usually utilized for urban natural gas pipeline material. In the United States and Europe, API 5L X42 and X52 are recommended in the ASME B31.12 code according to their high experiences in natural gas and hydrogen mixed transportation [7]. After years of research, there are some theories to explain the phenomenon of hydrogen embrittlement in materials, including the theory of hydrogen enhanced decohesion mechanism (HEDE) [8] and the theory of hydrogen enhanced local plasticity (HELP) [9]. However, due to the lack of sufficient test and operating data, the performance degradation mechanism of steel pipelines in contact with the hydrogen environment is still unclear; therefore, accidents may occur if existing pipelines are directly employed to transport HCNG.

At present, in order to simulate the hydrogen environment during the service process of materials, gaseous hydrogen charging method and electrochemical hydrogen charging method are often used in the hydrogen embrittlement studies of materials. Although the method of gaseous hydrogen charging under high pressure is closer to the service state of pipeline steel, the experiment is very difficult to conduct because of the expensive experiment cost and high experimental safety requirements. As a comparison, electrochemical hydrogen charging method is usually adopted to simulate a hydrogen environment and test resistance to hydrogen embrittlement of materials due to the high hydrogen charging efficiency and convenient operation [10–12]. As long as the hydrogen fugacity of electrochemical and gaseous hydrogen charging is the same, electrochemical hydrogen charging would be equivalent to gaseous hydrogen charging at a particular temperature and pressure [13].

Many scholars have scrutinized the hydrogen embrittlement characteristics of low carbon steel, austenitic stainless steel, and steel pipelines by employing the Slow strain rate tensile (SSRT) test and electrochemical permeation method. Hu et al. [14] conducted SSRT test to the samples of 2.25Cr–1Mo steel used for hydrogenation reactor and found the temper embrittlement gives rise to the reduction of the ductility of the material. Depover et al. [15] investigated the effect of hydrogen on the mechanical properties of generic Fe–C alloys by tensile tests, and presented that ductility of bainitic and martensitic materials both decreased by 20%, whereas the ductility of pearlitic and ferritic materials reduced about 50%. Martin et al. [16] studied the effect of the alloy elements on the material’s susceptibility to hydrogen embrittlement through tensile test, magnetic response measurements and thermodynamic calculations. Their results showed that the presence of hydrogen has little effect on the strength of the tested materials, while the decreasing austenite stability would cause the increasing of ductility loss. Yang et al. [17] researched the effect of hydrogen on the fracture behaviors of Incoloy alloy 825 by means of SSRT. Their results indicated that the ductility of the Incoloy alloy significantly decreased as the hydrogen charging current density increases in the process of hydrogen precharging. In the above tests, samples are all pre-charged with hydrogen, then the SSRT is carried out. These findings can only reflect the effect of internal hydrogen on pipeline steel. In order to study the effect of ambient hydrogen, it is necessary to use the dynamic hydrogen charging SSRT method. This method couples the permeation process of ambient hydrogen with the stress field, which is closer to the actual service conditions of the pipeline steels.

Thermal desorption spectroscopy (TDS) method is another important approach to examine the hydrogen embrittlement mechanism of materials. By analyzing the thermal desorption process and characteristics of hydrogen in the material, the distribution of hydrogen and hydrogen content in the material can be calculated, and the interaction law between hydrogen and the hydrogen trap of the material can be determined.

Takahagi et al. [18] used TDS method to study the hydrogen-induced surface free bond breakage on the semiconductor surface. Hadam et al. [19] employed TDS method to compare the distribution of hydrogen in the material after pre-charging with industrial pure iron and high carbon steel. Their results showed that the distribution of hydrogen along the thickness direction of the material is not uniform. By means of TDS test, Escobar et al. [20] analyzed the S550MC samples after electrochemical hydrogen charging, and found that the hydrogen charging samples had two desorption peaks, and the peak temperatures were concentrated at 70 °C and 140 °C, respectively. With the increase of hydrogen release time, the peak height of the curve of the low temperature peak gradually decreased. Lemus et al. [21] investigated the microstructure influence on hydrogen trapping in a Cr–Mo type steels through electrochemical permeation test, TDS, SEM and TEM analysis. Their results demonstrated that there is an extra-peak below 200 °C, which was attributed to the hydrogen trapping of vanadium carbide. Wang et al. [22] studied effect of quenching-tempering treatment on the hydrogen embrittlement resistance of a reactor pressure vessel steel and found that two hydrogen states were identified in the hydrogen desorption profiles and the high temperature peak is the irreversible hydrogen. Although the TDS method has been used to study the mechanism of hydrogen embrittlement, due to the dissimilarities in the microstructure and chemical compositions of various materials, hydrogen absorption properties, including the
hydrogen solubility and hydrogen permeability of each steel, are not the same [23, 24]. That means that the damage theory of hydrogen to pipelines steel is not perfect, and further research and verification studies are still required.

To further reveal the hydrogen embrittlement mechanism of materials and to find the suitable hydrogen-resistant steel pipelines for conveying natural gas blended with hydrogen, four typical pipeline steels, including X42, X52, X70, and AISI 1020 steel, are chosen as the research objects to inspect their mechanical properties variations in a hydrogen environment. The dynamic hydrogen charging SSRT method is employed to test the hydrogen resistance of materials comprehensively, and the mechanical performance degradation of each material is then carefully derived and displayed. Additionally, the TDS is exploited to describe the materials’ capabilities in capturing hydrogen. Combined with the SEM pictures of fractured tensile samples, the hydrogen embrittlement susceptibility of these steel pipelines is deeply discussed. The results of this paper reveal the performance degradation mechanism of pipeline steel in hydrogen environment more realistically, and provide a technical basis for the rational selection of HCNG pipeline steel.

2. Test facility and method

2.1. Test equipment and method

Figure 1 shows the SSRT test system in a dynamic hydrogen charging environment. It is mainly composed of three major parts: an SSRT machine, an electrochemical workstation, and a hydrogen environment box. The tensile sample and the platinum electrode are exploited as the cathode and anode, respectively. The test method adopts constant current polarization. The specimen is charged with hydrogen using CS 350 electrochemical workstation, and the properties of the specimen are tested with MFDL 100 slow strain rate tensile stress corrosion tester. During performing a tensile test on the hydrogen-charged sample, the hydrogen diffusion rate should be similar to the material strain rate to allow hydrogen to interact with dislocations completely. Hence, the slow strain rate tensile test is commonly implemented. The moving rate of the crosshead is 0.1 mm min$^{-1}$, and the corresponding strain rate is $5.4 \times 10^{-5}$/s. After conducting the tensile test, the fractured zone of the specimen is cut off and observed with the SEM. The hydrogen desorption curve is measured with a TDS analyzer, and the hydrogen concentration of each steel is then calculated.

Both the SSRT and TDS specimens are taken from the pipe’s axial direction. Figure 2 shows the geometry of the SSRT specimen, the thickness of the sample is 3 mm. The surfaces of the SSRT specimen are polished with 1000 grade SiC papers and then washed with acetone. The tensile specimens are sealed with silicone rubber except for the working surface to charge hydrogen.

In the SSRT experiment, it does not establish equilibrium conditions throughout the specimen. Hydrogen is charged while stretching (applied load), and the two are basically synchronized. Hydrogen charging continued until the sample is broken. This is also called the dynamic hydrogen charging process. Dynamic hydrogen charging is adopted to investigate the influence of external hydrogen on the properties of tensile specimens. The speed of the crosshead is set to 0.1 mm min$^{-1}$. The composition of the hydrogen charging electrolyte is 0.5 mol L$^{-1}$H$_2$SO$_4$ + 1.85 mmol l$^{-1}$Na$_4$P$_2$O$_7$. Researches shown that metal materials have a critical current density
that produces irreversible hydrogen damage under the conditions of electrochemical hydrogen charging. For pipeline steel, the critical value is between 10 and 30 mA cm\(^{-2}\) [14]. In order to ensure the integrity of the experimental results, the current density of hydrogen charging in the test is set in the range of 0 \textendash 20 mA cm\(^{-2}\), which include 0, 1, 2.5, 5, 10 and 20 mA cm\(^{-2}\). The zero current density corresponds to the sample subjected to a tensile test with a slow strain rate in the air environment at room temperature, as the uncharged control group.

To improve the accuracy of the test results, three tests are carried out at each current density, and the average value of the performed three tests is taken when calculating the tensile properties of the material. The original data gotten from the tensile test is the change of the tensile load in terms of the crosshead displacement. In order to make the material performance display more universal, load-displacement curve is converted into the nominal stress-strain curve of each material through calculations and corrections.

The TDS experimental device is mainly composed of four parts: a vacuum high temperature test environment box, a mass spectrometer, a pump system, and a data acquisition system. Among them, the ultra-high vacuum high temperature test environment box is composed of a vacuum chamber, a sample loading chamber and a working platform integrated with each component of the system. With the employment of resistance wire heating, the heating rate of the sample stage in the vacuum chamber can be automatically controlled by the program. In the TDS test, the specimen is a smooth round bar of dimensions 25 mm \(\times\) \(\Phi\) 5 mm. Considering the TDS test has high requirements for the finished surface of materials, the sample hence should be polished step by step with 200\# to 2000\# sandpapers. After polishing, TDS specimens are immersed in 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) + 1.85 mmol L\(^{-1}\) Na\(_4\)P\(_2\)O\(_7\) aqueous solutions while hydrogen is charged at the current density of 1 mA cm\(^{-2}\) with the charging time of 48 h. To prevent hydrogen from escaping, the TDS test is conducted immediately after hydrogen charging. The samples are heated from room temperature to 700 °C in the TDS vacuum chamber with a heating rate of 100 °C/h. The hydrogen escape rate and its concentration are then measured by a mass spectrometer.

### 2.2. Test materials

The test materials are taken from different gas transmission pipes, including X42, X52, X70, and AISI 1020. In order to reveal the fundamental reasons for the resulted discrepancy in the hydrogen resistance of various types of steel pipelines, chemical composition and metallographic structure of pipeline consisting materials are systematically tested. Chemical compositions of all steels are measured by spark source atomic spectrum based on the Chinese standard GB/T 9711-2017, and the specific values of constituent parts of materials have been provided in table 1. After cutting from the pipe base material, the metallographic specimens are prepared through grinding, polishing, and finally etching with 4% nitric acid alcohol at the polished surface. The microstructure of each material is then observed under the optical microscope (OM), as demonstrated in figure 3.

In figure 3, the length direction (horizontal) of each sub-picture corresponds to the circumferential direction of the pipeline, and the width direction (longitudinal) of each sub-picture corresponds to the thickness direction of the pipeline. It can be seen from figure 3 that the microstructures of X42, X52 and AISI 1020 steel are both

### Table 1. Chemical compositions of understudy test steels (wt%).

| Steel | C   | Si  | Mn  | P   | S   | Cr  | Mo  | Ni  | Nb  | V   | Cu  | Al  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| X42   | 0.063 | 0.19 | 1.26 | 0.0098 | 0.0034 | 0.021 | 0.0017 | 0.011 | 0.017 | 0.0035 | 0.019 | 0.038 |
| X52   | 0.13  | 0.26 | 1.06 | 0.0072 | 0.0068 | 0.050 | 0.026 | 0.045 | 0.0019 | 0.033 | 0.087 | 0.028 |
| X70   | 0.064 | 0.21 | 1.47 | 0.0078 | 0.002 | 0.027 | 0.010 | 0.028 | 0.022 | 0.013 | 0.023 | 0.029 |
| AISI 1020 | 0.19  | 0.25 | 0.54 | 0.015 | 0.013 | 0.053 | 0.0078 | 0.039 | 0.0017 | 0.0027 | 0.14  | 0.0019 |
composed of pearlite (P) and ferrite (F). Among them, AISI 1020 steel has the largest ferrite grain size, ferrite grain size of X52 steel is in the middle, and X42 steel has the smallest ferrite grain size. This is due to the difference in alloying element content in each steel. The metallographic structure of X70 is composed of granular bainite (B) and martensite (M), which is displayed in figure 3(C).

3. Results and discussion

3.1. Dynamic hydrogen charging SSRT analysis

The tensile test is widely employed for testing the mechanical performance of materials. In the present scrutiny, the strength and plasticity indexes of each material, including ultimate tensile strength (UTS), yield strength (YS), elongation after rupture (EL), and reduction of area (RA), are measured by dynamic hydrogen charging SSRT. During the SSRT test, the raw data obtained from the test is the curve of tensile load as a function of cross-head displacement. However, in order to make the material performance display more universal, the relationship between load and displacement has been transformed into the relationship between stress and strain in SSRT experimental research. In addition, in order to ensure that the obtained engineering strain of the tested material during the tensile process is reliable, some corrections are performed in the process of transforming the load-displacement curve to the stress-strain curve, which focusing on stripping the influence of the elastic deformation (displacement) of the fixture on the total deformation (displacement) of the specimen. For materials without obvious yield steps (such as low alloy steel X70), in order to measure the yield characteristics of the material, it is specified that the stress value corresponding to 0.2% plastic strain is used as the material yield strength.

The effect of hydrogen charging on the tensile behavior of the material has been presented in figure 4. It can be seen that, except in the case of X70 whose results are given in figure 4(c), the total elongation pertinent to the fractured state of the tensile samples after dynamic hydrogen charging is significantly lower than that of the samples without hydrogen charging. For instance, the total elongation associated with the X42 fracture state is about 45% during stretching in the air, while the total elongation at the fractured state after hydrogen charging at various current densities is in the range of 25%-35%. This issue clearly proves that X42 has good plasticity.
without hydrogen charging, and the hydrogen charging would significantly reduce the total elongation, particularly at the fracture mode of the material. For the case of X70, the total elongation at the fractured state during stretching in the air is only about 20%, mainly attributed to the poor plasticity of the material. The hydrogen concentration in the material is more likely to reach the saturation level after hydrogen charging. As a result, the total elongation associated with the fracture of X70 does not change significantly under various current densities of the SSRT test.

Additionally, it can be observed from the demonstrated plots in figure 4 that the tensile curves of each material under various current densities would basically overlap in the elastic deformation stage. This issue indicates that dynamic hydrogen charging has almost a trivial influence on the mechanical properties of the material in the elastic stage. Nevertheless, by arriving at the plastic stage, the plotted curves show a particular discrepancy, which shows that the dynamic hydrogen charging significantly influences the plasticity and strength of the material.

Figure 5 shows the effect of the current density on the plasticity and strength of various steel pipelines. As can be seen, compared with the YS of the material before hydrogen charging, the YS of these four materials are usually enhanced after hydrogen charging, which is consistent with previous studies [15, 25]. This fact is mainly due to the interaction of dissolved hydrogen in the steel gap with dislocation to form the Cottrell atmosphere, which increases dislocation resistance [26]. After hydrogen charging, the UTS of X42, X52, and X70 are all enhanced because the solution strengthens the role of dissolved hydrogen. In contrast, the UTS of AISI 1020 is significantly reduced. This is because hydrogen reduces the grain boundary binding energy. The grain boundary of AISI 1020 is particularly sensitive to hydrogen; therefore, its ability to withstand deformation would be dramatically lessened, causing dislocation to slip early. From macroscopic points of view, such a state is initiated by entering the material’s tensile curve to the necking stage in advance. From the results in figure 5, it can be seen that although the tensile strength of different pipeline steels tends to increase or decrease in the hydrogen environment, the overall change is not large. Within the range of hydrogen charging current density tested in this paper (0 ~ 20 mA cm⁻²), the maximum difference between the tensile strength of X42, X52, X70 and AISI 1020 under hydrogen charging conditions and the tensile strength under air environment is 1.7%, 6.4%, 3.7% and 9.8%, respectively. Therefore, it can be considered that the effect of hydrogen charging on the strength of pipeline steel is small.

Figure 4. Tensile curve of each test material for various current density levels: (a) X42; (b) X52; (c) X70; (d) AISI 1020.
The influence of hydrogen charging on the plasticity index of each material is somehow similar. As the current density rises, the EL and RA reduce. For each considered material, as the current density increases, the plasticity significantly reduces first and then tends to level off. This fact reveals that when the hydrogen concentration in the material inclines to be saturated, the degradation effect of hydrogen on the material also tends to stabilize. Further observations display that the variation range of the RA is more pronounced than that of the EL after hydrogen charging. For a more systematic investigation of the engineering problem, hydrogen embrittlement (HE) index $I_A$ is defined as follows:

$$I_A = \frac{A_0 - A_H}{A_0} \times 100\%$$

where $A_0$ and $A_H$ in order are the RA of the uncharged and charged specimen. This index can be effectively exploited for sensitivity analysis of materials to the hydrogen embrittlement.

The change of the HE index for each material in terms of the current density has been demonstrated in figure 6. It can be observed that the HE index of each material generally grows by an increase in the current density. Among the four steel pipelines mentioned above, the lowest and highest HE indexes are detectable for the cases of X42 and AISI 1020, respectively.

In order to further reveal the performance degradation mechanism of different pipeline steels in the presence of hydrogen, in this paper, on the basis of obtaining the law of the mechanical properties of pipeline steels with the hydrogen charging current density, the scanning electron microscope (SEM) is used to further observe and analyze the tensile fracture morphology of various pipeline steels materials under dynamic charging conditions. The essence of fracture is that the bonding force between atoms is destroyed, and plastic fracture is microporous aggregation fracture. When the material is stretched to produce plastic deformation, stress concentration occurs locally in the material. The stress destroys the bonding force between atoms, and firstly forms micropores, that is, the source of cracks. As the plastic deformation continues, the micropores continue to expand and merge due to the presence of three-dimensional stress concentration, and finally form dimples. Therefore, the larger the dimples, the stronger the local anti-instability of the material and the better the plasticity.

Figure 7 presents the fracture morphology of specimens exposed to the air using the SEM. It can be seen that the fracture of different materials exposed to the air are all specified by dimples. The number, size, and depth of dimples for each material are different, determined by the material’s composition and structure.
In order to show more clearly the microscopic morphology changes in the central zone and the marginal zone of the tensile fracture of each pipeline steel under different dynamic hydrogen charging current densities, figures 8–11 present the fracture morphology of specimens charged hydrogen at various levels of the current density using the SEM. The fracture morphology of the central zone for each material has been demonstrated in figures 8(a), 9(a), 10(a), and 11(a) at the hydrogen charging current density of 1 mA cm$^{-2}$. The initiated fractures in X42, X52, and X70 are still dominated by dimples, but these are apparently less and shallower comparing with the fracture under air stretching condition; The morphology of the central zone of AISI 1020 is significantly different from X42, X52, and X70, and its surface presents a mixed morphology composed of relatively flat
‘cleavage-like’ facets, micropores and tearing edges. This fracture mode is called ‘quasi-cleavage’ fracture. Compared with the central zone, the fracture morphology of the marginal zone (figures 8(b), 9(b), 10(b), and 11(b)) shows a more noticeable brittleness. The appeared fractures in the X42 and X52 are lamellar cleavage and stepped cleavage, the cleavage plane of the X70 is relatively flat, while AISI 1020 presents the typical cleavage feature with a river-like pattern. The caused fracture in AISI 1020 consists of staggered cleavage planes with large secondary cracks and almost no dimples, representing that a significant brittle fracture occurs for the case of AISI 1020 at the current density of 1 mA cm$^{-2}$. When the current density increases to 10 mA cm$^{-2}$, the central zone of each material (figures 8(c), 9(c), 10(c), and 11(c)) appears as quasi-cleavage morphology composed of the mixture of dimples and cleavage planes. For all considered materials, the marginal zone at 10 mA cm$^{-2}$ (figures 8(d), 9(d), 10(d), and 11(d)) presents a more severe brittle fracture than that at 1 mA cm$^{-2}$.

It is clear from the SEM image that the fracture mode of materials significantly changes after hydrogen charging. In the present study, the whole fracture of the specimen can be divided into the central and marginal zones, which are mainly distinguished by various fracture morphologies. Hydrogen generates on the surface of the material during charging, and it takes a particular time for hydrogen to permeate from outside to inside. Therefore, the hydrogen concentration gradually decreases from outside to inside. Brittle fracture characteristics can be apparently observed in the marginal zones, such as secondary cracks (figure 8(b)) or river-like pattern (figure 11(b)). Due to the low hydrogen concentration in the central zone, it reveals certain ductile fracture characteristics, such as shallow dimples (figure 8(a)) and quasi cleavage features (figure 9(a)). The essence of the dimple is the cavity formed by the dislocation in the discontinuity of the matrix during the stretching process. In the process of cavity nucleation and growth, transverse shear force accelerates the aggregation of cavities, thereby forming shallow dimples, so the fracture in the central area presents a quasi-cleavage morphology with a certain residual toughness.

3.2. TDS analysis

Figure 12 shows the hydrogen desorption curves of the understudy steel pipelines. According to the plotted results, there exist two distinct hydrogen desorption peaks for each material. For low temperatures, the peaks of the plots associated with AISI 1020, X52, and X42 are the highest, lower, and lowest levels. The high-temperature
peaks of X42, X52, and X70 approximately take place at the same temperature, while the temperature

corresponds to the high-temperature peak of AISI 1020 is significantly lower than that of other steel pipelines.

Subsequently, the accumulation of hydrogen can be readily calculated by integration. By this view, the hydrogen

concentration for X42, X52, X70, and AISI 1020 are obtained as 0.28, 0.65, 0.65, and 1.63 ppm, respectively.

The peaks of hydrogen desorption curves in the TDS test are generated from hydrogen traps of various

binding energies. If the microstructure of the material becomes complicated, the solubility of hydrogen at each

hydrogen trap would be significantly different, yielding multiple peaks on the curve. It can be seen from

figure 12, the curve associated with each carbon steel exploited in this test presents two peaks. According to the

literature [27], the hydrogen absorption peak at the ferrite-pearlite interface in carbon steel occurs at 116 °C;

hence, the demonstrated low-temperature peak in figure 12 corresponds to the reversible hydrogen trap at the

ferrite-pearlite interface. The area enclosed by the curve and the horizontal axis characterizes the level of

hydrogen concentration, indicating that the grain boundaries of these kinds of steel pipelines have significant
differences in the solubility of hydrogen. The hydrogen solubility decreases as one moves from AISI 1020 to X52,
then X70, and finally X42. This finding confirms that the hydrogen concentration at the low-temperature peak is
strictly related to the grain boundary between ferrite and pearlite. For low-carbon-based steels, the higher the
carbon content, the higher the pearlite content. As a result, the grain boundary area between pearlite and ferrite
also increases. This conclusion can also be proved from the chemical composition and microstructure of tested
steel pipelines. According to table 1, the carbon content of materials reduces as one shifts from AISI 1020 (0.19%) to X52 (0.13%), and then X42 (0.063%). Figures 3(a), (b), and (d) present that from X42 to AISI 1020, pearlite content does increase, the corresponding grain volume increases, and thereby, the solubility of hydrogen at the grain boundary magnifies. The metallographic structure of the X70 is somehow different from that of the other three materials, and its grain boundary cannot be clearly defined; hence, X70 does not participate in the comparison study mentioned above. However, it is detectable from figure 12 that the corresponding temperature to the low-temperature peak of X70 is significantly higher than that of other materials. This issue is mainly attributed to the fact that X70 contains a large amount of martensite, resulting in higher dislocation density. According to previous investigations [28], the binding energy of dislocations is commonly higher than

![Figure 9. SEM morphology of the caused fracture in X52 specimen: (a) central zone, the current density of 1 mA cm$^{-2}$; (b) marginal zone, the current density of 1 mA cm$^{-2}$; (c) central zone, the current density of 10 mA cm$^{-2}$; (d) marginal zone, the current density of 10 mA cm$^{-2}$.](image-url)
that of the ferrite-pearlite interface. Therefore, the hydrogen desorption temperature of dislocations is higher than that of grain boundaries.

According to figure 12, the high-temperature peak corresponds to the irreversible hydrogen trap at particles or impurities in the second phase, commonly caused by hydrogen desorption of irreversible hydrogen traps with large binding energy [28]. The irreversible hydrogen traps in steel are mainly alloy element compounds. According to the literature [29], MnS is the main harmful impurity in low-carbon steel. The MnS is a strong irreversible hydrogen trap. As seen from table 1, Mn is the main strengthening element in steel pipelines. The Mn content is about 1.26% in X42, 1.06% in X52, 1.47% in X70, but only 0.54% in AISI 1020 steel. Figure 10 presents that the temperature pertinent to the high-temperature peaks of X42, X52, and X70 are similar, while the temperature of the high-temperature peak of AISI 1020 is seemingly lower. Therefore, it can be concluded that the high-temperature peaks of X42, X52, and X70 are essentially caused by Mn. The high-temperature peak of X70 is the highest among others because it contains the largest Mn. Although the Mn content in X42 is slightly higher than that in X52, the S content in X52 is twice that in X42, resulting in a little discrepancy between the high-temperature peaks of these two materials. Comparing with the other three materials, the Cu content (0.14%) in AISI 1020 steel is higher. According to the studies from Shi et al [30], dispersed fine Cu-rich phases in matrix can act as the beneficial hydrogen traps, which helps to avoid the localized high concentration of hydrogen. Therefore, the high-temperature peak of AISI 1020 steel may be caused by the hydrogen trap formed by Cu.

3.3. Discussion

Comprehensive analysis on the dynamic hydrogen charging SSRT results and SEM of fracture morphology in section 3.1 show that, due to the high concentration of hydrogen in the marginal zone, dislocations lead to the formation of cracks (for instance, see secondary cracks in figure 8(d)). Under action of the hydrogen enhanced decohesion mechanism (HEDE) [8], brittle cleavage fracture occurs in the marginal zone. Then the crack gradually propagates inward, resulting in the material’s capability to withstand significantly reduced loads. Under action of the hydrogen enhanced local plasticity (HELP) mechanism [9], rapid tearing occurs in the central zone, forming a mixed morphology with both toughness and brittleness. As the current density grows,

Figure 10. SEM morphology of the caused fracture in X70 specimen: (a) central zone, the current density of 1 mA cm$^{-2}$; (b) marginal zone, the current density of 1 mA cm$^{-2}$; (c) central zone, the current density of 10 mA cm$^{-2}$; (d) marginal zone, the current density of 10 mA cm$^{-2}$.
the embrittlement degree of fracture enlarges. It implies that the general trend of the morphological transformation is shifted from the ductile fracture to the transitional quasi-cleavage fracture, and finally to the cleavage fracture.

TDS results in section 3.2 show that, there are differences in the solubility of hydrogen for different types of pipeline steels, and this difference is related to the factors including microstructure, element composition of the materials, et al. For the three ferritic steels of X42, X52 and AISI 1020, the low temperature peaks on the TDS curve correspond to the reversible hydrogen traps formed at the interface between ferrite and pearlite, and the

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**Figure 11.** SEM morphology of the caused fracture in AISI 1020 specimen: (a) central zone, the current density of 1 mA cm\(^{-2}\); (b) marginal zone, the current density of 1 mA cm\(^{-2}\); (c) central zone, the current density of 10 mA cm\(^{-2}\); (d) marginal zone, the current density of 10 mA cm\(^{-2}\).

**Figure 12.** Hydrogen desorption curve of test materials.
higher the C content in the steel, the higher the hydrogen concentration in the grain boundaries. For the martensitic steel of X70, the high-density dislocation martensitic structure will form irreversible hydrogen traps, causing the hydrogen concentration to increase. For X42, X52 and X70, the harmful impurity MnS formed by Mn and S elements is a strong irreversible hydrogen trap, which can also cause hydrogen aggregation. These results mean that we can preliminarily screen out the pipes that may have good hydrogen resistance by examining the chemical composition, metallographic structure and grain size of the candidate pipeline steels.

Considering that X52 steel has been widely used in hydrogen transmission systems, from the application point of view, it can be considered that X52 has sufficient resistance to hydrogen-induced deterioration. It is therefore reasonable to select X52 as a benchmark to screen other materials. Therefore, the C content in the candidate pipeline steel should not exceed the C content in X52 (0.13%). In order to reduce strong irreversible hydrogen traps such as MnS, the S content and Mn content in the steel should not exceed the S content (0.0068%) and Mn content (1.06%) in X52 steel. The high-density dislocations formed by martensite are strong hydrogen traps, which are highly sensitive to hydrogen, and the plasticity of martensitic steel is poor, so it is not suitable for natural gas mixed hydrogen transportation pipes. Ferrite is the most common structure in pipeline steel, and its susceptibility to hydrogen embrittlement depends on the ferrite grain size in addition to the content of alloying elements. The grain sizes of the ferritin pipeline steel used in this study are 8.6 μm (X42), 16.2 μm (X52) and 35.6 μm (AISI 1020). The results of the dynamic hydrogen charging SSRT test show that the HEI of AISI 1020 is much higher than that of X42 and X52, so the HEI of the material has a certain correlation with the grain size, that is, the larger the grain size, the higher the HEI, the worse the hydrogen resistance of the material. Therefore, when selecting pipe steel, it should be ensured that the ferrite grain size is at least less than 35 μm. If conditions permit, the ferrite grain size can be further refined to the level of X52 steel (16.2 μm). The dynamic hydrogen charging SSRT test can be used to evaluate the deteriorating effect of environmental hydrogen on the plasticity of the material. The hydrogen embrittlement index of X52 at a current density of 1 mA cm⁻² is 50%, when the HEI of the candidate material is less than 50%, its resistance to hydrogen embrittlement is considered qualified.

4. Conclusions

In this paper, the mechanical properties of X42, X52, X70, and AISI 1020 in the presence of a hydrogen environment were obtained through dynamic hydrogen charging SSRT test. The fracture patterns were then investigated by SEM, and the relationship between microstructure and macro-mechanical properties was established. Moreover, the vital role of the alloy elements in hydrogen embrittlement was also revealed by the TDS analysis. The crucially obtained findings from this research work are as follows:

1. Both values of EL and RA were reduced by increasing the current density, and the reduction of RA is more pronounced than that of the EL. The yield strength and tensile strength of X42, X52, and X70 have a slight increase after hydrogen charging. The YS of AISI 1020 strengthens after hydrogen charging, while the UTS gradually decreases with the growth of the current density. YS and UTS variation range of the four steels before and after hydrogen charging is within 10%. The HE index indicates that AISI 1020 has the highest hydrogen embrittlement susceptibility, then X70, and X42 has the lowest one.

2. Fracture of tensioned specimens indicates that the cleavage area of the marginal zone is larger than that of the central zone. As the current density grows, the fracture mode transforms from the ductile fracture to the quasi-cleavage fracture and finally turns into the cleavage fracture. The hydrogen embrittlement fracture of the tensile specimen results from the action of the HEDE and HELP in various zones.

3. For the three ferritic steels of X42, X52 and AISI 1020, the higher the C content, the higher the hydrogen concentration in grain boundaries. For the martensitic steel of X70, the accumulation of dissolved hydrogen originates from the high density of dislocations formed by the martensitic structure. For X42, X52, and X70, the high temperature peak on the TDS curve corresponds to the strong irreversible hydrogen traps formed by Mn compounds, and the higher the Mn content in the steel, the higher the hydrogen concentration in the irreversible hydrogen traps.

4. A simple evaluation method for the selection and evaluation of natural gas-hydrogen mixed pipes is proposed. The C content in the candidate pipeline steel should not exceed 0.13%, and the corresponding S content and Mn content should not exceed 0.0068% and 1.06%, respectively. Martensitic steel is not suitable for HCNG pipes. For ferritin pipeline steel, the HEI of the material has a certain correlation with the grain size, and it should be ensured that the ferrite grain size is at least less than 35 μm. Furthermore, in order to ensure that the hydrogen embrittlement resistance of the material is qualified, the HEI of the candidate material should less than 50%.
The results of this paper reveal the hydrogen embrittlement mechanism of pipeline steel in service environment more realistically, and provide a technical basis for the rational selection of HCNG pipeline steel.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

**Declaration of interest statement**

The authors declared that there is no conflict of interest.

**Data availability**

All data generated or analyzed during this study are included in this published article and the referenced papers.

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