

# 掺氢天然气环境下管道钢氢脆行为研究进展

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**摘要:** 为推动我国掺氢天然气管道的发展, 综述了目前含氢气环境下管道钢氢脆的研究成果, 总结了温度、压力、掺氢比等运行条件对钢材氢脆的影响, 分析了钢材强度、微观组织、氢陷阱等材料性质与管道钢氢脆行为之间的联系, 归纳了预防和抑制管道钢氢脆行为的方法。笔者认为, 当前亟待解决的科学技术问题包括进一步探究掺氢天然气管道环境下不同运行条件对管道钢氢脆行为的影响规律; 确定掺氢天然气管道的安全运行温度、压力、掺氢比等关键参数; 建立不同服役条件下掺氢天然气管道输送的安全评价方法, 完善掺氢天然气管道与现役管道相容性评价体系; 形成掺氢天然气管道的设计规范和相关标准; 开展气体抑制剂和阻氢涂层等抗氢脆方法的评价。

**关键词:** 掺氢天然气; 管道钢; 氢脆; 机理; 掺氢比; 涂层

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## Research Progress on Hydrogen Embrittlement Behavior of Pipeline Steel in the Environment of Hydrogen-Blended Natural Gas

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**ABSTRACT:** Hydrogen energy has been vigorously developed in recent years, but excessive transportation and storage costs have become a key issue in restricting the development of hydrogen utilization. Blending H<sub>2</sub> into existing natural gas long-distance pipelines is the potential best way to transport hydrogen on a large scale, cost-effectively and efficiently. However, H<sub>2</sub> can induce hydrogen embrittlement of pipeline steel, which seriously restricts the safe operation of hydrogen-blended natural gas

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pipelines.

In order to promote the development of hydrogen-blended natural gas pipelines in China, this paper reviews the current research results of hydrogen embrittlement of pipeline steel in hydrogen-containing environment; summarizes the influence of operating conditions such as temperature, pressure, and hydrogen blending ratio on hydrogen embrittlement of steel; analyzes the relationship between the material properties and the hydrogen embrittlement behavior of pipeline steel, such as strength, microstructure organization, hydrogen traps; summarizes the methods to prevent and inhibit the hydrogen embrittlement behavior of pipeline steel.

For the high-pressure hydrogen-blended natural gas pipeline, the operating parameters such as temperature, pressure, and hydrogen-blending ratio have a great impact on the hydrogen embrittlement. At present, there are few studies focusing on the effect of temperature on the hydrogen embrittlement of pipeline steel. With the increase in hydrogen partial pressure, the hydrogen embrittlement susceptibility of pipeline steel increases. Affected by the service life and materials of the pipeline, the ranges of the safe hydrogen blending ratio obtained by different researches are quite different. It is necessary to determine the safe hydrogen blending ratio suitable for the hydrogen-blended natural gas pipelines in China, and formulate relevant standards and specifications.

Steel properties are also an important factor affecting the hydrogen embrittlement behavior. Most studies have shown that hydrogen embrittlement susceptibility of pipeline steel increased with strength, but the quantitative relationship is not clear. The different microstructures of steels can also lead to different hydrogen embrittlement susceptibilities, and particularly, there is a higher hydrogen embrittlement sensitivity for the welding area. In addition, under different conditions, the effects of hydrogen traps such as dislocations and grain boundaries on the hydrogen embrittlement behavior of steel are different, and further research is needed.

Finally, three methods for inhibiting hydrogen embrittlement of pipeline steel are summarized, including changing phase structure, blending protective gas, and hydrogen barrier coating. But all three methods have great limitations. Changing the phase structure may lead to the decline of the mechanical properties of some materials, and the energy consumption is large, so it is not suitable for large-scale application in long-distance pipeline steel. For blending protective gas, the influence of different gases on the hydrogen embrittlement behavior of steel is still controversial, and its mechanism of action is not completely clear. Moreover, blending other gases will have a greater impact on the safety of pipeline operation and downstream user terminals. The hydrogen barrier coating will cause severe local corrosion after damage. Due to the limitation of price and processing technology, the hydrogen barrier coating cannot be applied on a large scale.

In conclusion, the current scientific and technical issues that need to be solved include: further exploring the influence of different operating conditions on the hydrogen embrittlement behavior of pipeline steel under the environment of hydrogen-blended natural gas pipelines; determining the key parameters of hydrogen-blended natural gas pipelines such as the safe operating temperature, pressure and hydrogen blended ratio; establishing safety evaluation methods for hydrogen-blended natural gas pipeline transportation under different service conditions, and improving the compatibility evaluation system of hydrogen-blended natural gas pipelines and existing pipelines; forming design specifications and related standards for hydrogen-blended natural gas pipelines; carrying out evaluation of anti-hydrogen embrittlement methods such as gas inhibitors and hydrogen barrier coating.

**KEY WORDS:** hydrogen-blended natural gas; pipeline steel; hydrogen embrittlement; mechanism; hydrogen blending ratio; coating

在化石能源日渐枯竭、全球气候恶化的趋势下, 各国都在大力发展低碳可再生清洁能源<sup>[1-2]</sup>。我国国家发展改革委印发的《能源技术革命创新行动计划(2016—2030年)》中, 已将太阳能、风能、氢能等清洁能源的开发利用作为下一阶段的重点任务, 重点指出要大力发展氢气的低成本制造、运输以及储存。由于可再生能源发电具有不稳定性, 且电量供应受到市

场供需的影响, 造成了大量风电、光电的资源浪费<sup>[3-4]</sup>。将不稳定的风电、光电等通过电解制成氢气后, 再进行运输和利用是解决以上问题的有效途径<sup>[5-7]</sup>。然而, 目前基础设施、运输方式等因素的限制, 导致氢气的运输和储存成本过高, 成为氢气在现有能源供应体系中未得到广泛应用的重要原因<sup>[8]</sup>。目前, 包括我国在内的很多国家都已经建立了大规模的天然气输送管

道,利用现有的天然气管道网络,向天然气中添加氢气,并混合输送,就可以在较低的成本下实现氢气的大规模输送<sup>[9-10]</sup>。截至目前,多个国家都已开展了掺氢天然气管道示范工程<sup>[11]</sup>,表1汇总了近年来国内外主要的掺氢天然气管道项目,图1总结了掺氢天然气管道所涉及的环节以及关键问题。从图1和表1可以看出,氢气的掺入一方面会引入氢气掺混、液化及分离等新的工艺;另一方面,氢气区别于天然气的物理性质,也会对管道安全、管输设备的相容性、管道的完整性等提出新的要求。与欧美发达国家相比,我国掺氢天然气管道的发展目前仍处在起步阶段,需要解决氢气掺入所带来的一系列关键问题,制定针对掺氢天然气管道建设及运行的相关标准规范。

钢材在氢气环境下会产生氢损伤,包括氢脆、氢致裂纹、氢鼓泡等,此外在较高的温度压力下还会发生脱碳和氢蚀。其中氢脆是发展掺氢天然气管道输送技术的主要安全问题。当管道钢处在富氢环境中时会发生氢脆现象,造成管道钢延性和疲劳强度的降低,甚至导致管道开裂,引发严重的安全问题<sup>[20-21]</sup>。管道

钢在氢气环境中发生氢脆的根本原因是氢原子对钢材的渗透。氢原子渗透进入钢材诱发氢脆并产生裂纹的过程为<sup>[9,22]</sup>:氢气分子在与管道内壁碰撞的过程中吸附在管道钢表面,并分解为吸附氢原子;吸附氢原子扩散到管道钢内部成为溶解氢原子,并在钢材内部迁移以及缺陷和微裂纹尖端聚集;当氢原子积累到一定程度后,会引起管道钢脆化,并进一步产生氢致裂纹。目前氢气加剧钢材性能劣化的主流机理有:氢压理论、氢致弱键理论以及氢致局部塑性变形理论等<sup>[23-28]</sup>。尽管目前国内外对氢脆机理已经进行了大量的研究,但针对不同的材料或外部条件,氢气的影响机制不同<sup>[29]</sup>,同时某一特定氢脆现象可能受多种不同机制共同作用<sup>[30]</sup>,控制脆化现象和失效的实际微观机制仍需进一步探索<sup>[31-32]</sup>。

本文对目前含氢气环境下管道钢氢脆研究进行了系统的综述,总结分析了管道运行工况、钢材性质等不同因素对管道钢氢脆行为的影响,归纳了预防和抑制管道钢氢脆行为的方法,并针对现有研究的不足,提出了当前亟待解决的科学技术问题 and 研究展望。

表 1 国内外主要的掺氢天然气输送管道示范项目

Tab.1 Demonstration projects of hydrogen-blended natural gas pipelines at home and abroad

Demonstration Project	Country/Region	Hydrogen blended ratio/%	Time
NATURALHY <sup>[12-13]</sup>	Europe	0-50	2004—2009
Sustainable Ameland <sup>[14]</sup>	Netherlands	5-20	2008—2011
GRHYD <sup>[15]</sup>	France	6-20	2014—2019
Avacon <sup>[16]</sup>	Germany	20	2019
CONTURSI <sup>[17]</sup>	Italy	5-10	2019
Chaoyang Hydrogen Blending Demonstration Project <sup>[18]</sup>	China	5	2019
HyDeploy <sup>[19]</sup>	Britain	20	2020

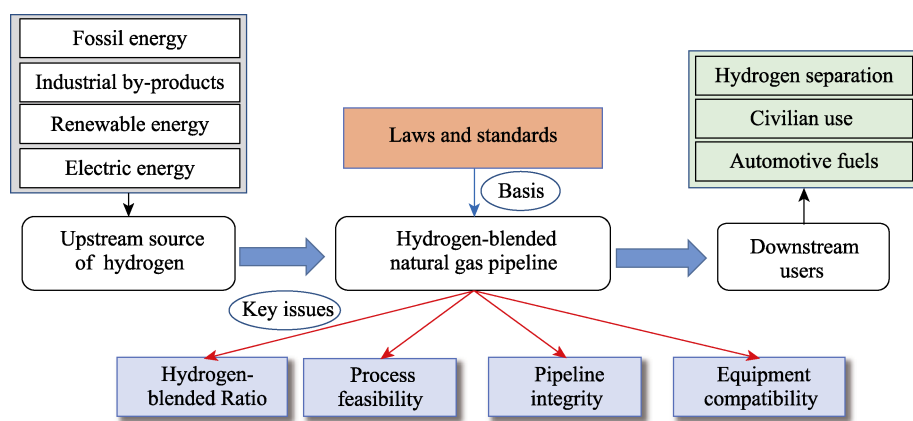


图 1 掺氢天然气管道主要环节和涉及的关键问题

Fig.1 Main processes and key issues of hydrogen-blended natural gas pipelines

## 1 掺氢天然气管道钢氢脆行为影响因素

为保证掺氢天然气管道的安全运行,需明确影

响管材氢脆行为的主要因素。在高压掺氢天然气长输管道中,管道运行工况(温度、总压、氢气分压)以及管材状态(金相组织、析出物杂质、缺陷等),都会对氢气与管道钢之间的相互作用产生较大的影响<sup>[32-34]</sup>。

## 1.1 运行条件

### 1.1.1 温度的影响

温度的变化会影响氢原子的扩散和聚集, 从而影响钢材的氢脆行为。目前, 几乎没有针对气相环境下温度对管道钢氢脆行为影响的相关研究, 但现有的其他钢材在液相环境下的氢脆研究仍具有重要指导意义。Mehta 等<sup>[35]</sup>在早期的研究中发现, 当温度从室温上升到 150 °C 后, 氢原子扩散速率以及氢致裂纹的扩展速率会明显加快。Doshida 等<sup>[36]</sup>也得到了类似的结论, 当温度大于 -30 °C 后, 钢的氢脆敏感性随温度的升高而增加。然而温度对钢材氢脆行为的影响还存在争议。近期的研究中, Xing 等<sup>[37]</sup>分别在模拟地层溶液环境和空气环境中对 X90 钢进行慢应变速率拉伸试验, 并发现 X90 钢的氢脆行为存在温度阈值, 且氢脆敏感性不随温度单调变化。X90 钢在 313 K 下的氢脆敏感性最高; 当温度低于 313 K 时, 氢脆效应随温度的升高而增强; 超过 313 K 时, 氢脆效应随温度的升高而减弱。Momotani 等<sup>[38]</sup>研究了低碳马氏体钢氢脆敏感性在 -100~100 °C 内随温度的变化情况, 将试样在液相环境中电化学充氢 24 h 后进行拉伸试验。结果表明, 在 0~100 °C 内, 含氢试样的抗拉强度和伸长率随温度降低而降低; 当温度降到 0 °C 以下时, 抗拉强度和伸长率又逐渐增加。最终得出, 当温度处在室温下时, 低碳马氏体钢的氢脆的敏感性最大。

以上研究表明, 温度的变化可能对氢脆行为存在较为显著的影响。从热力学的角度分析, 低温环境会使得氢原子的渗透、扩散变慢, 很难发生富集; 在高温条件下, 氢原子的活化能和扩散速率高, 使得氢原子不易在位错、晶界等处富集, 甚至发生热解吸现象, 使金属内部氢原子浓度降低<sup>[38-39]</sup>, 同时, 在高温环境下金属表面生成的氧化膜也会抑制氢脆行为<sup>[40]</sup>。总体上, 目前关于温度对常用管线钢氢脆行为影响的研究还较少, 尤其是在掺氢天然气输送环境下, 不同季节管输温度变化对氢气在管道钢中扩散聚集的影响, 以及不同钢材的安全输送温度的确定都需要更进一步的研究。

### 1.1.2 压力的影响

1) 纯氢环境下氢气压力的影响。近年来有很多研究者通过在纯氢气环境中进行试验来探究氢气压力对管道钢氢脆行为的影响。Amaro 等<sup>[27,41]</sup>分别对 X52 钢和 X100 钢在氢气环境下进行了拉伸试验和疲劳裂纹扩展试验。研究表明, 与空气环境下相比, 13.8 MPa 高压氢气环境下, 2 种钢材拉伸试样的伸长率都明显减小, 韧性损失显著。在一定的应力强度因子范围内, X52 和 X100 钢的疲劳裂纹扩展速率随氢气压力的增加而增加。当氢气压力从 1.72 MPa 增加到 20.68 MPa 后, X100 钢的疲劳裂纹扩展速率提高 2 倍, 甚至 1 个数量级。Stalheim 等<sup>[42]</sup>和 San 等<sup>[43-44]</sup>评估了在 5.5~

21 MPa 的氢气环境下, 不同种类的 X60、X70、X80 管道钢的氢脆敏感性。研究结果表明, 与空气环境下相比, 5.5 MPa 氢气环境下, 每种管道钢拉伸试样的断面收缩率和断裂韧性都显著减小, 钢材的氢脆程度增加, 但随着压力的进一步增大至 21 MPa, 钢材的断面收缩率和断裂韧性减小幅度较小。同时, 在较大的强度因子范围内 ( $\Delta K_{\max} > 20 \text{ MPa} \cdot \text{m}^{1/2}$ ), 当氢气压力从 5.5 MPa 增加至 21 MPa 后, 试样疲劳裂纹的扩展速率变化不大。Andrew 等<sup>[45]</sup>在 1.7、7、21、48 MPa 等 4 种氢压力下, 对 X52 和 X100 管道钢进行了疲劳裂纹扩展试验。结果表明, X100 和 X52 在氢气环境下的疲劳裂纹扩展速率比在空气中高出 1~2 个数量级, 且在一定的强度因子范围内, 裂纹增长速率随着氢气压力的增加而增大。

此外, 还有研究表明, 氢气对管材的劣化影响并不会随着压力的升高而一直增大, 而是存在一个临界压力值。Alvaro 等<sup>[46]</sup>研究了 X70 钢焊接热影响区在 20 °C 高压氢气环境下的氢脆敏感性, 在不同氢压力 (0.1、0.6、10、40 MPa) 下进行了单边缺口试样的拉伸试验, 同时对断裂韧性进行了量化。结果表明, 当氢气压力高于 0.1 MPa 时, 试样的断裂韧性明显降低; 当氢压力达到 0.6 MPa 以上后, 断裂韧性没有继续减小。他们进一步指出, X70 钢焊接热影响区发生氢脆现象的临界压力在 0.1~0.6 MPa。类似地, Moro 等<sup>[47]</sup>在不同氢气压力下对 X80 钢进行了拉伸试验, 并通过断面收缩率对氢脆敏感性进行量化。结果表明, 当氢气压力超过 10 MPa 后, X80 钢的氢脆敏感性将不再受到压力升高的影响。

在氢气环境中, 氢原子在铁等金属中的溶解度与氢气压力的平方根成正比<sup>[48]</sup>。在一定范围内, 单位体积内压力越高, 氢气分子的浓度越高, 氢气分子与管道内壁碰撞分解为氢原子的几率就会增大, 进而使得氢原子在管道钢中的溶解度增大<sup>[47]</sup>, 导致钢材内部裂纹尖端具有更高的氢浓度<sup>[49]</sup>, 促进脆化的发生。以上研究结果表明, 对于不同的管道钢材料, 压力对氢脆敏感性的影响规律, 以及发生氢脆的临界压力阈值尚不明确, 还需要进行进一步的研究。

2) 掺氢环境下氢气分压的影响。在掺氢天然气管道中, 氢气分压可通过式 (1) 确定:

$$p_{\text{H}} = \alpha p \quad (1)$$

式中:  $p_{\text{H}}$  为氢气分压;  $\alpha$  为掺氢比例;  $p$  为总压。

显然, 掺氢比例和总压的变化都会改变氢气分压的大小。张体明<sup>[50]</sup>测量了 X80 钢在 12 MPa 模拟煤制气环境 (0.25 MPa 氢气, 0.20 MPa 二氧化碳, 其余为氮气) 中的氢渗透电流密度。结果表明, 在反应釜中充入 0.25 MPa 的氢气后, 氢渗透电流迅速增大, 电流稳定后再依次充入二氧化碳和氮气将压力逐级提高至 12 MPa, 这个过程中稳态电流基本不会变化, 如图 2 所示。张体明认为, 氢渗透电流的大小仅与煤

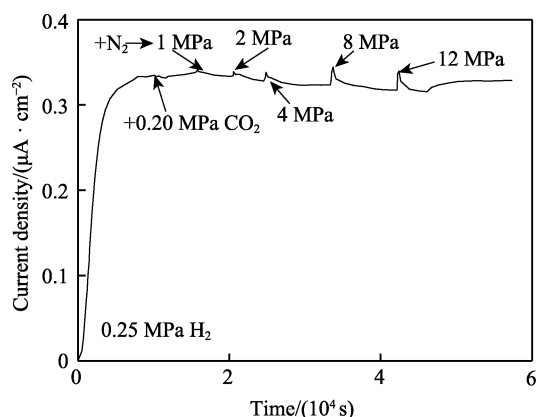


图2 X80钢在模拟煤制气环境中分段加压过程中氢渗透曲线<sup>[50]</sup>

Fig.2 Hydrogen permeation curve of X80 steel during staged pressurization in coal gas environment<sup>[50]</sup>

制气中的氢分压有关，与总压关系不大。类似地，Nguyen等<sup>[51]</sup>在5、7、10 MPa等3种典型压力下（掺氢比分别为0.1%、0.5%、1%、3%、5%、100%）的甲烷/氢气混合气体中对X70钢的力学性能进行了测试。结果表明，X70钢的力学性能下降主要受到氢气分压而非总压的影响，如图3所示。

对于掺氢天然气管道而言，在管输压力一定的情况下，氢气在管道中的分压是通过掺氢比来确定的。近年来也有学者在掺氢环境下对钢材氢脆行为影响进行了相关研究。An等<sup>[52]</sup>通过低周疲劳试验和裂纹扩展试验探究了在总压12 MPa掺氢环境下不同氢分压对X80氢脆敏感性的影响。研究表明，随着氢气分压的增加，X80缺口试样的疲劳循环次数迅速减小，而紧凑拉伸试样的裂纹扩展速率则急剧增加。与在氮气环境中相比，0.2 MPa的氢气分压下，X80钢的疲劳失效循环次数下降20%，疲劳裂纹扩展速率增加7倍；当氢气分压进一步增加至8 MPa后，失效循环次数的下降幅度达到90%，疲劳裂纹扩展速率增加2倍。An进一步指出，随着氢气压力的增加，裂纹扩展速率增加是X80钢疲劳寿命降低的主要原因。

Meng等<sup>[53]</sup>研究了12 MPa下含0~50%（体积分数）氢气的天然气/氢气混合气体对X80管线钢力学性能的影响。结果表明，随着氢气含量的增加，X80钢的氢脆敏感性升高，疲劳裂纹扩展速率明显加快。类似地，在最新的研究中，Nguyen等<sup>[51,54]</sup>同样发现，在5~10 MPa的压力下，X70钢的氢脆敏感性随着掺氢比的增大而增大，且氢气的体积分数达到0.7%的时候，X70钢的断裂模式会由韧性断裂向脆性断裂转变。

尽管目前国内外学者的研究都表明氢气分压越高，钢材的氢脆敏感性就越高，但是对于影响管道安全运行的临界氢气分压，目前尚没有统一的定论。赵德辉等<sup>[55]</sup>将X70钢和20#钢的母材金相试样和焊接区U弯试样放置在总压12 MPa的氮气/氢气混合环境中（其中氢气分压2 MPa）1个月后，未发现氢损伤和氢致开裂现象，同时外加恒载荷的试样也未发生氢致开裂，并进一步得到X70钢和20#钢在煤制天然气（总压为12 MPa，氢气分压为0.72 MPa）中长期服役不会发生氢致开裂及氢损伤。关鸿鹏等<sup>[56]</sup>研究发现，X70钢的母材和焊缝试样在总压为4 MPa、氢气分压为0.2 MPa的煤制气环境下，冲击性能、塑性及材料的损伤容限均未受到显著影响。然而，同样在12 MPa的总压工况下，也有研究表明，当氢气分压分别为0.72 MPa<sup>[57]</sup>和0.96 MPa<sup>[58]</sup>时，X80钢都表现出一定的氢脆敏感性。

此外，由于氢气和甲烷的性质不同，天然气掺氢后不仅会对管材性能产生影响，还会对管道的完整性、管输设备以及下游用户终端产生影响<sup>[59]</sup>。对于天然气管道掺入氢气而不影响管道安全和下游终端的临界值，不同的研究给出了不同的结论，包括3%<sup>[12]</sup>、10%<sup>[21]</sup>、17%<sup>[60]</sup>、20%<sup>[13]</sup>，甚至50%<sup>[13]</sup>。国际能源署（IEA）在2020年更新了不同国家对天然掺氢比例的限制<sup>[61]</sup>，如图4所示（特殊工况分别是，德国：未与管网连接的CNG加气站；立陶宛：压力大于1.6 MPa的天然气管道；荷兰：高热值煤气）。国外已有一些

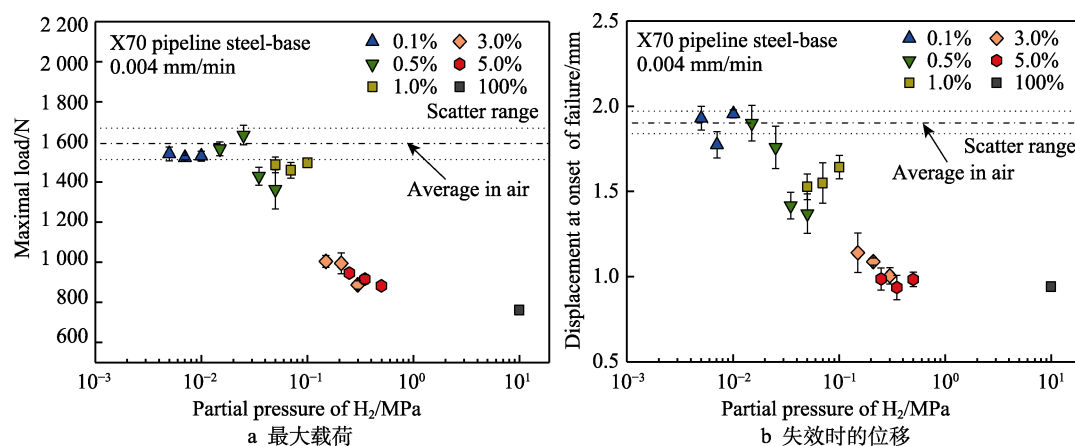


图3 不同工况下氢气分压对X70钢力学性能的影响<sup>[51]</sup>

Fig.3 Influence of partial pressure of hydrogen on X70 steel<sup>[51]</sup>: a) maximal load; b) displacement at failure onset



标准规范对特定情况下天然气管道的掺氢比作出了限制, 美国机械工程师协会颁布的 ASME B31.12-2014 “Hydrogen Piping and Pipelines” 适用于氢气体积分数不小于 10% 的情况。标准指出, X60 及以上管道的设计压力不应大于 10 MPa。当掺入 10% 以上的氢气后, 还需要根据标准中给出的校核方法重新计算最大操作压力。除此之外, 还有欧洲标准 CGA-5.6 “Hydrogen Pipeline System”, 其中针对使用 X52 钢的天然气管道的掺氢比例限制为 10%。

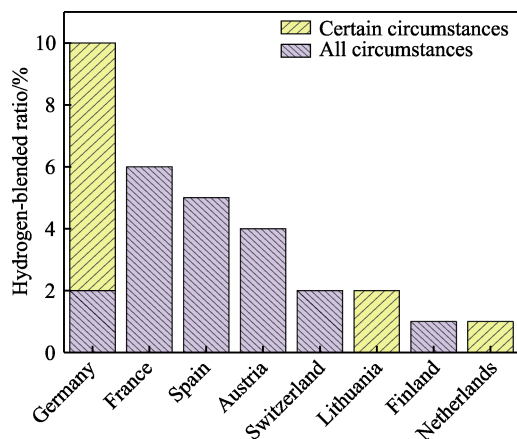


图 4 国际能源署发布的不同国家对掺氢天然气管道中氢气含量的限制<sup>[61]</sup>

Fig.4 Limits on hydrogen blending in natural gas networks in certain countries<sup>[61]</sup>

综上所述, 目前国内外虽然已开展掺氢天然气管道的安全掺氢比研究, 但仍缺乏一致的结论。对于在役的天然气管道来说, 受管道服役年限、材料的影响, 不同研究所得出的安全掺氢比范围有较大不同。国内尚缺乏掺氢天然气管道的安全掺氢比标准规范, 需确定在管输压力下不同掺氢比对管道力学性能的影响, 同时结合管输设备相容性、用户需求及经济性等多方面因素, 确定适用于我国掺氢天然气管道的安全掺氢比, 填补相关规范标准的空白。

## 1.2 材料性质

### 1.2.1 强度的影响

目前, 多数研究者认为, 钢材的氢脆敏感性会随着强度的增大而增大<sup>[31]</sup>, 对于抗拉强度小于 700 MPa 的钢, 几乎不会出现严重的氢脆问题<sup>[62]</sup>。Nanninga 等<sup>[49]</sup>和 Hardie 等<sup>[63]</sup>研究表明, 不同管道钢的氢脆敏感性随着强度的增加而增大。Andrew 等<sup>[45]</sup>也指出, 相较于 X52 钢, X100 钢疲劳裂纹的扩展速率和随着氢气压力的增加而增大的现象更加明显。Komatsuzaki 等<sup>[64]</sup>指出, 当碳钢屈服强度由 500 MPa 升至 1 400 MPa 后, 氢致断裂的应力阈值显著降低, 最大降幅甚至达到 70%。然而, Cabrini 等<sup>[65]</sup>认为, 当钢材的极限抗拉强度超过 700 MPa 后, 氢脆敏感性才会随着极限抗拉强度的增大而增大; 极限抗拉强度小于 700 MPa

时, 钢材的氢脆敏感性反而会随着极限抗拉强度的增大而降低。一般认为, 低级别强度的管道钢的韧性相对较高, 抗氢脆性能也较好。欧洲目前所建立的工业级口径氢气管道中, 大部分都使用 X42、X52、X56 等低强度管线钢, ASME B31.12—2014 也推荐采用 X42、X52 等低强度钢<sup>[66]</sup>。

尽管目前大多数的研究表明强度的提升会增加钢材的氢脆敏感性, 但对于常用管道钢氢脆敏感性与强度之间的定量关系尚不明确, 还需结合金属相态组成及晶粒大小等微观因素进行分析。同时, 掺氢比对管材强度与氢脆敏感性之间关系的影响也需要进一步的探究。

### 1.2.2 微观组织的影响

钢材的微观金相组织是影响钢材氢脆的关键因素<sup>[67]</sup>。目前, 输气管道常用管道钢 (X70、X80 等) 的金相组成以铁素体为主。Stalheim 等<sup>[68]</sup>测试了 X52、X60、X70、X80 管道钢在 5.5、20.7 MPa 氢气环境中的断裂韧性, 结果表明, 多边形铁素体/针状铁素体组织抗氢性能略优于多边形铁素体/上贝氏体-珠光体组织。类似地, Davani 等<sup>[69]</sup>和 Zhao 等<sup>[67]</sup>也指出, X60、X80 管线钢中针状铁素体对氢致裂纹的敏感性较低。针状铁素体较好的抗氢脆性能, 是由于其较高的韧性能够抑制裂纹的扩展<sup>[70]</sup>。除了铁素体外, 在管道钢的加工焊接等过程中, 还会引入少量的马氏体、贝氏体以及奥氏体等组织, 这些相组织都会对钢材的氢脆敏感性产生影响。其中, 马氏体对氢原子的捕获能力最强, 且马氏体更容易受到氢脆的影响<sup>[71-72]</sup>, 这归因于马氏体含有较多的位错和边界缺陷, 会导致氢致裂纹的快速萌生和扩展<sup>[73]</sup>。此外, 贝氏体对氢脆的敏感性也高于铁素体<sup>[70,74]</sup>。奥氏体组织的氢脆敏感性最低, 这是由于氢在奥氏体中溶解度高, 且氢原子在奥氏体中的扩散速率比马氏体慢 3~4 个数量级<sup>[75]</sup>。Tao 等<sup>[76]</sup>研究指出, 大多数氢致裂纹会在奥氏体处停止发展。然而, 一直增加奥氏体的含量并不能提高钢的抗氢脆性能, 因为在高氢浓度和应力集中的耦合作用下, 奥氏体会转变为马氏体, 进而增加氢脆敏感性<sup>[77]</sup>。

长输管道在焊接过程, 较高的温度造成焊接部位组织的不均匀分布, 导致焊缝部位的氢脆敏感性更高。美国 Sandia 国家实验室<sup>[78]</sup>测量了 X52、X65、X70 等钢材在 6.9 MPa 的氢气环境下的拉伸性能, 结果表明, 焊缝处塑性的劣化比母材更严重。张体明等<sup>[79]</sup>研究表明, X80 钢焊缝部分晶粒明显长大, 大角度晶界含量减少, 氢的扩散速率及其在裂纹尖端的富集程度增加, 导致焊缝部分的氢脆系数相较于母材明显升高。

对于同种牌号的钢, 国内外对成分的控制以及热加工工艺会有所差别, 所以对于国外的实验结果并不能盲目采用<sup>[80]</sup>, 还需要进一步明确本土钢材不同组织的抗氢脆性能, 建立失效评价准则。

### 1.2.3 陷阱的影响

在钢材的内部会不可避免地存在位错、相界面、微孔以及各种杂质析出物,这些结构或者夹杂物的周围会产生应力集中,从而诱导氢原子发生聚集<sup>[81]</sup>。这种可以吸附氢原子的结构或者夹杂物通常被称为氢陷阱。根据其与氢原子之间结合能的大小,一般将结合能小于 60 kJ/mol 的氢陷阱定义为可逆氢陷阱。当氢原子进入可逆陷阱后,在一定的条件(高温等)下,可以逃逸出来。结合能大于 60 kJ/mol 的氢陷阱为不可逆氢陷阱,一旦氢原子进入不可逆氢陷阱,将难以离开<sup>[82]</sup>。表 2 总结了一些常见的结构和杂质析出相与氢原子之间的结合能。

表 2 金属中不同结构/夹杂物与氢原子之间的结合能  
Tab.2 The binding energy between structures/inclusions and hydrogen atoms in steel

Hydrogen trap	Binding energy/(kJ·mol <sup>-1</sup> )	Reference
Dislocation	18–44	[83–86]
Grain boundaries	9.6–72	[83–84,86–88]
Micro-Voids	27.6–29.1	[85–86]
NbC	39–68	[87]
TiC	46–110	[88–89]
Al <sub>2</sub> O <sub>3</sub>	79	[90]
NbN	23–24	[87]

氢陷阱对于钢材氢脆行为的影响,学术界目前还没有形成统一的结论。有研究表明,不可逆氢陷阱不仅可以束缚氢原子,还能阻碍位错运动,从而抑制氢脆行为<sup>[91]</sup>;而可逆氢陷阱的存在,使得溶解在钢中的可扩散氢浓度升高,会加剧钢材的氢脆现象<sup>[77,82,92]</sup>。Huang 等<sup>[93]</sup>和 Nakatani 等<sup>[94]</sup>则认为,被不可逆陷阱捕获的氢原子会加剧高强度钢力学性能的劣化。一方面,氢陷阱可以阻碍氢原子的渗透,降低氢脆敏感性;另一方面,氢陷阱附近也可能出现氢原子过多聚集,萌生裂纹<sup>[95]</sup>,且氢陷阱密度也会对钢材氢脆敏感性产生较大的影响<sup>[96]</sup>。在不同的条件下,氢陷阱对钢材氢脆行为的作用效果也会有所不同,需要进行进一步的研究。

除了钢材本身的结构缺陷以外,钢材中氧化物、铁碳化物等析出夹杂物也是诱发氢脆的常见氢陷阱<sup>[97]</sup>。Xue 等<sup>[81]</sup>发现, X80 钢中的氢致裂纹主要萌生在富 Si、富 Al 的夹杂物附近。Escobar 等<sup>[98]</sup>研究表明, MnS 夹杂物会促进氢致裂纹的扩展,而 MnS 析出物是否会对钢材的氢脆行为产生影响还存在争议<sup>[99]</sup>。除此之外,管线钢的氢脆敏感性还和 C<sup>[100]</sup>、S<sup>[101]</sup>、V<sup>[102]</sup>等杂质有关。夹杂物的尺寸和分布也会对氢脆行为产生影响,一般来说,夹杂物的尺寸和分布面积越大,越容易萌生氢致裂纹<sup>[103–104]</sup>。

综上所述,无论是结构缺陷,还是杂质析出相,氢陷阱对于钢材氢脆敏感性的影响还存在一定争议。

同时,目前的研究大多数通过电化学液相充氢的方法来表征氢陷阱,对于将来的掺氢天然气管道来说,高压气相环境下管线钢中氢陷阱对氢脆行为的影响是否会发生变化,还需要更进一步的研究。

## 2 氢脆的预防措施分析

### 2.1 改变微观相组织

由于不同微观金相组织的氢脆敏感性差异较大,可以通过优化热处理工艺和处理参数获得理想的组织,晶粒细化工艺也可以提高钢的抗氢脆性能<sup>[105]</sup>。Enyinnaya 等<sup>[106]</sup>比较了 2 种不同相组织的 X70 管线钢的抗氢脆性能,结果表明,含有更多马氏体/残余奥氏体成分的 X70 钢具有更好的抗氢致裂纹的性能。类似地, Ohaeri 等<sup>[107]</sup>将 X70 钢进行了两步退火处理后,产生了铁素体–回火马氏体双相组织,虽然强度降低,但是由于回火马氏体较小的晶粒尺寸减缓了氢在钢中的迁移率,使得 X70 钢的氢脆敏感性降低。Park 等<sup>[70]</sup>评价了经过不同热处理后 X65 钢的抗氢脆性能,结果表明,针状铁素体的高韧性会阻止裂纹的扩展,钢材的抗氢脆性能也会随着针状铁素体含量的提升而提高。但改变相组织可能会导致部分材料力学性能下降,且控制工艺复杂,能耗大<sup>[108]</sup>,将来是否可以大规模应用于长输管道钢还有待进一步的验证。

### 2.2 气体抑制剂

氢气环境中的某些气体有抑制钢材氢脆倾向的作用。Liu 等<sup>[109]</sup>和 Jacobs<sup>[110]</sup>等发现, SO<sub>2</sub> 和 CO<sub>2</sub> 作为“毒化剂”可以抑制氢原子向钢材内部的渗透,从而降低钢材的氢脆程度。Deimel 等<sup>[111]</sup>和 Kussmaul 等<sup>[112]</sup>发现了氢气环境下 O<sub>2</sub> 的存在同样会降低钢的氢脆效应。Michler 等<sup>[113]</sup>研究表明, O<sub>2</sub> 对于氢脆的抑制作用是 O<sub>2</sub> 分压的函数,同时抑制氢脆的 O<sub>2</sub> 分压存在临界值,根据钢材等级和温度变化,分压临界值可能相差 3 个数量级。这种现象是由于 O<sub>2</sub> 可以使得裂纹尖端钝化,阻止氢原子渗透,但是随着裂纹的扩展,新的裂纹尖端表面并不能被完全钝化,从而导致 O<sub>2</sub> 对氢脆的抑制作用下降<sup>[114]</sup>。CO 通过抑制钢材表面的氢吸附,从而抑制管道钢氢脆行为。李婷婷<sup>[115]</sup>研究发现,在 10 MPa 的氢气环境下,添加 0.01 MPa 分压的 CO 就使得 X80 钢的氢脆指数降低 95%以上。

在最新的研究中, Shang 等<sup>[116]</sup>发现, CO<sub>2</sub> 和 H<sub>2</sub> 会产生耦合作用,从而增加钢的氢脆敏感性。除此之外,水蒸气也会对促进钢材的氢脆行为<sup>[117]</sup>,不仅如此, CO<sub>2</sub><sup>[118]</sup>和 H<sub>2</sub>S<sup>[119]</sup>等组分会和水共同形成酸性环境,也会对加剧管道钢的氢脆现象。

就目前的研究来看,不同气体对于钢材氢脆行为的影响还存在争议,其作用机理尚不完全明确,需要在掺氢天然气管道实际工况条件下进一步探究不同

气体对于长输气体管道钢氢脆行为的影响。同时, 诸如分压阈值、不同气体之间的耦合作用等问题也都需要进一步的实验来验证, 同时结合管道运行安全和管道下游需求, 最终确定可以添加到管道中的氢脆气体抑制剂, 这将对掺氢天然气管道的发展具有重要意义。

## 2.3 阻氢涂层

除了加入抑制气体和改善管道钢微观组织结构之外, 阻氢内涂层由于可以阻止氢原子的渗透, 也成为预防管道钢氢脆的新方法<sup>[9,20]</sup>。阻氢涂层大致上分为: 金属涂层、金属氧化物涂层以及石墨烯等非金属涂层。很早就有研究者发现, 在钢表面电镀上 Pt、Ni、Sn、Cd 等金属薄膜可以降低氢原子的渗透效率<sup>[120-121]</sup>, 但是金属涂层常常因为断裂应变过低、附着力不足和涂层缺陷等问题使得涂层失效, 需要进一步改进涂层工艺来改善涂层延性、附着力等性能<sup>[122]</sup>。

金属涂层可以抑制氢原子渗透, 一部分原因归结于其表面的氧化层<sup>[123]</sup>, 金属氧化物也是一种有效的阻氢涂层。在金属氧化物涂层中,  $\text{Al}_2\text{O}_3$  的阻氢效果较好, 1  $\mu\text{m}$  厚的  $\text{Al}_2\text{O}_3$  可以使氢渗透通量下降 3~4 个数量级, 而且其在高温下也具有较好的稳定性<sup>[124-125]</sup>。相较于单层的氧化物涂层, 复合涂层具有更好的阻氢效果、更好的结合强度以及稳定性<sup>[126-127]</sup>。然而, 并不是所有的氧化物都可以起到阻氢的作用, 其对氢脆的影响在很大程度上取决于氧化物的深度分布, 晶粒尺寸以及堆积方式, 只有特定的氧化物层才有较好的阻氢效果<sup>[128]</sup>。

随着石墨烯材料的兴起, 其阻氢性能的研究近年来也得到了广泛关注。由于氢原子进入石墨烯涂层后, 会形成 C—H  $\text{sp}^3$  键, 从而阻碍了氢原子的渗透, 在金属表面覆盖石墨烯涂层后, 金属内部的氢含量会显著降低<sup>[129]</sup>。C—H 的形成引起了石墨烯结构的变形, 导致其阻氢能力降低。通过调整合成方式进一步减小晶粒尺寸, 改善石墨烯结构以及多层石墨烯的研制可以进一步提升石墨烯涂层的抗变形能力<sup>[130]</sup>。

虽然涂层的阻氢效果好, 但是由于涂层在加工过程中本身就会引入一些氢原子, 而且其在破损后还会引发严重的局部腐蚀, 再加上经济性以及加工工艺的限制, 导致阻氢涂层并不能大规模应用<sup>[108]</sup>。目前的研究多采用液相充氢实验来衡量阻氢涂层的效果, 并不能真实反映其在氢气环境中的阻氢效果, 还需要在高压气相环境中展开抗氢脆效果的评价研究。此外, 新型涂层材料以及新型涂层制备工艺的效果评价也需进一步探究。

## 3 结语

基于以上综述分析, 现阶段对于掺氢天然气管道的氢脆行为研究较少, 不同服役条件下掺氢天然气管道的风险性、安全性和可靠性的变化规律尚不明确。

针对当前的研究现状, 为推动将来掺氢天然气管道的发展, 提出以下建议及展望:

1) 目前温度变化对氢原子的扩散聚集以及常用管线钢氢脆行为的影响规律尚无定量描述, 需通过试验明确不同钢材在掺氢天然气管道输送环境下的安全输送温度。

2) 掺氢天然气管道的安全掺氢比缺乏一致的结论。需研究在管输压力下不同掺氢比对管道材料性能的影响, 确定管材发生氢脆的临界压力阈值, 同时结合管输设备相容性、用户需求及经济因素等多方面条件, 最终确定适用于我国掺氢天然气管道的安全掺氢比。

3) 改善微观组织、在管道中添加气体抑制剂、添加阻氢涂层等抑制管道钢氢脆行为的方法需要进一步探索, 尤其需要明确实际管输温度压力、不同气体相互作用等因素对阻氢效果的影响。

4) 目前我国尚缺乏掺氢天然气管道建设和安全运行的相关规范, 应尽快建立不同服役条件下掺氢天然气管道输送的安全评价方法, 形成相关标准规范, 为掺氢天然气管道的发展和大规模应用奠定基础。此外, 还需完善掺氢天然气管道与现役天然气管道相容性的评价方法和评价体系。

## 参考文献:

- [1] 邱玥, 周苏洋, 顾伟, 等. “碳达峰、碳中和”目标下混氢天然气技术应用前景分析[J]. 中国电机工程学报, 2022, 42(4): 1301-1321.  
QIU Yue, ZHOU Su-yang, GU Wei, et al. Application Prospect Analysis of Hydrogen Enriched Compressed Natural Gas Technologies under the Target of Carbon Emission Peak and Carbon Neutrality[J]. Proceedings of the CSEE, 2022, 42(4): 1301-1321.
- [2] 李秋扬, 赵明华, 张斌, 等. 2020 年全球油气管道建设现状及发展趋势[J]. 油气储运, 2021, 40(12): 1330-1337.  
LI Qiu-yang, ZHAO Ming-hua, ZHANG Bin, et al. Current Construction Status and Development Trend of Global Oil and Gas Pipelines in 2020[J]. Oil & Gas Storage and Transportation, 2021, 40(12): 1330-1337.
- [3] 张世钦. 基于改进粒子群算法的风光水互补发电系统短期调峰优化调度[J]. 水电能源科学, 2018, 36(4): 208-212.  
ZHANG Shi-qin. Short-Term Peak Shaving for Wind-Photovoltaic-Hydro System Optimization Based on Improved Particle Swarm Optimization[J]. Water Resources and Power, 2018, 36(4): 208-212.
- [4] 张歆萌, 黄炜斌, 王峰, 等. 大型风光水混合能源互补发电系统的优化调度研究[J]. 中国农村水利水电, 2019(12): 181-185.  
ZHANG Xin-shuo, HUANG Wei-bin, WANG Feng, et al. Research on the Optimal Scheduling of Large Wind-PV-Hydro Hybrid Energy Complementary Power Gener-



- ation System[J]. China Rural Water and Hydropower, 2019(12): 181-185.
- [5] STILLER C, BÜNGER U, MØLLER-HOLST S, et al. Pathways to a Hydrogen Fuel Infrastructure in Norway[J]. International Journal of Hydrogen Energy, 2010, 35(7): 2597-2601.
- [6] RIVEROS-GODOY G A, CAVALIERO C, SILVA E. Analysis of Electrolytic Hydrogen Production Models and Distribution Modes for Public Urban Transport: Study Case in Foz do Iguaçu, Brazil[J]. International Journal of Energy Research, 2013, 37(10): 1142-1150.
- [7] RIVAROLO M, MARMI S, RIVEROS-GODOY G, et al. Development and Assessment of a Distribution Network of Hydro-Methane, Methanol, Oxygen and Carbon Dioxide in Paraguay[J]. Energy Conversion and Management, 2014, 77: 680-689.
- [8] HANLEY E S, DEANE J, GALLACHÓIR B Ó. The Role of Hydrogen in Low Carbon Energy Futures-a Review of Existing Perspectives[J]. Renewable and Sustainable Energy Reviews, 2018, 82: 3027-3045.
- [9] 李守英, 胡瑞松, 赵卫民, 等. 氢在钢铁表面吸附以及扩散的研究现状[J]. 表面技术, 2020, 49(8): 15-21.  
LI Shou-ying, HU Rui-song, ZHAO Wei-min, et al. Hydrogen Adsorption and Diffusion on Steel Surface[J]. Surface Technology, 2020, 49(8): 15-21.
- [10] WITKOWSKI A, RUSIN A, MAJKUT M, et al. Analysis of Compression and Transport of the Methane/Hydrogen Mixture in Existing Natural Gas Pipelines[J]. International Journal of Pressure Vessels and Piping, 2018, 166: 24-34.
- [11] EDWARDS R L, FONT-PALMA C, HOWE J. The Status of Hydrogen Technologies in the UK: A Multi-Disciplinary Review[J]. Sustainable Energy Technologies and Assessments, 2021, 43: 100901.
- [12] SUZUKI T, KAWABATA S, TOMITA T. Present Status of Hydrogen Transport Systems Utilizing Existing Natural Gas Supply Infrastructures in Europe and the USA[J]. IEEEJ, 2005(10): 1-16.
- [13] The NATURALHY Project: First Step in Assessing the Potential of the Existing Natural Gas Network for Hydrogen Delivery[J]. Unión Médica Du Canada, 2008, 114(3): 213-219.
- [14] KIPPERS M J, DE LAAT J C, HERMKENS R J M, et al. Pilot Project on Hydrogen Injection in Natural Gas on Island of Ameland in the Netherlands[J]. International Gas Research Conference Proceedings, 2011, 2: 1163-1177.
- [15] None. McPhy Energy Role in French Power-to-Gas GRHYD Programme[J]. Fuel Cells Bulletin, 2014, 2014(2): 9-10.
- [16] Fuel Cells Works. Hydrogen Levels in German Gas Distribution System to Be Raised to 20 Percent for the First Time[EB/OL]. (2019-08-3) [2021-07-13]. <https://fuelcellworks.com/news/hydrogen-levels-in-german-gas-distribution-system-to-be-raised-to-20-percent-for-the-first-time>.
- [17] SNAM: Hydrogen Blend Doubled To 10% in Contursi Trial[EB/OL]. (2020-01-18) [2021-07-13]. [https://www.snam.it/en/Media/news\\_events/2020/Snam\\_hydrogen\\_blend\\_doubled\\_in\\_Contursi\\_trial.html](https://www.snam.it/en/Media/news_events/2020/Snam_hydrogen_blend_doubled_in_Contursi_trial.html).
- [18] 中国能源报. 天然气掺氢技术距商用还有多远?[EB/OL]. (2020-09-28) [2021-07-13]. China Energy News. How Far is Natural Gas Hydrogen Technology from Commercial Use? [EB/OL]. (2020-09-28) [2021-07-13]. [http://paper.people.com.cn/zgnyb/html/2020-09/28/content\\_2011720.htm](http://paper.people.com.cn/zgnyb/html/2020-09/28/content_2011720.htm).
- [19] ITM Power. HyDeploy: UK Gas Grid Injection of Hydrogen in Full Operation[EB/OL]. (2020-01-02) [2021-07-13]. <https://www.itm-power.com/news/hydeploy-uk-gas-grid-injection-of-hydrogen-in-full-operation>.
- [20] DWIVEDI S K, VISHWAKARMA M. Hydrogen Embrittlement in Different Materials: A Review[J]. International Journal of Hydrogen Energy, 2018, 43(46): 21603-21616.
- [21] REITENBACH V, GANZER L, ALBRECHT D, et al. Influence of Added Hydrogen on Underground Gas Storage: A Review of Key Issues[J]. Environmental Earth Sciences, 2015, 73(11): 6927-6937.
- [22] SEREBRINSKY S, CARTER E A, ORTIZ M. A Quantum-Mechanically Informed Continuum Model of Hydrogen Embrittlement[J]. Journal of the Mechanics and Physics of Solids, 2004, 52(10): 2403-2430.
- [23] LYNCH S P. Gaseous Hydrogen Embrittlement of Materials in Energy Technologies[M]. Amsterdam: Elsevier, 2012: 274-346.
- [24] THOMAS S, OTT N, SCHALLER R F, et al. The Effect of Absorbed Hydrogen on the Dissolution of Steel[J]. Heliyon, 2016, 2(12): e00209.
- [25] KAPPES M, IANNUZZI M, CARRANZA R M. Hydrogen Embrittlement of Magnesium and Magnesium Alloys: A Review[J]. Journal of the Electrochemical Society, 2013, 160(4): C168-C178.
- [26] LU G, ZHANG Q, KIOUSSIS N, et al. Hydrogen-Enhanced Local Plasticity in Aluminum: An Ab Initio Study[J]. Physical Review Letters, 2001, 87(9): 095501.
- [27] AMARO R L, RUSTAGI N, FINDLEY K O, et al. Modeling the Fatigue Crack Growth of X100 Pipeline Steel in Gaseous Hydrogen[J]. International Journal of Fatigue, 2014, 59: 262-271.
- [28] TIEGEL M C, MARTIN M L, LEHMBERG A K, et al. Crack and Blister Initiation and Growth in Purified Iron Due to Hydrogen Loading[J]. Acta Materialia, 2016, 115: 24-34.
- [29] ROBERTSON I M, SOFRONIS P, NAGAO A, et al. Hydrogen Embrittlement Understood[J]. Metallurgical and Materials Transactions B, 2015, 46(3): 1085-1103.
- [30] ROBERTSON I M. The Effect of Hydrogen on Dislocation Dynamics[J]. Engineering Fracture Mechanics, 2001, 68(6): 671-692.
- [31] VENEZUELA J, LIU Qing-long, ZHANG Ming-xing, et al. A Review of Hydrogen Embrittlement of Martensitic

- Advanced High-Strength Steels[J]. Corrosion Reviews, 2016, 34(3): 153-186.
- [32] VERGANI L, COLOMBO C, GOBBI G, et al. Hydrogen Effect on Fatigue Behavior of a Quenched&tempered Steel[J]. Procedia Engineering, 2014, 74: 468-471.
- [33] SAINI N, PANDEY C, MAHAPATRA M M. Effect of Diffusible Hydrogen Content on Embrittlement of P92 Steel[J]. International Journal of Hydrogen Energy, 2017, 42(27): 17328-17338.
- [34] HOOSHMAND ZAFERANI S, MIRE SMAEILI R, POURCHARMI M K. Mechanistic Models for Environmentally-Assisted Cracking in Sour Service[J]. Engineering Failure Analysis, 2017, 79: 672-703.
- [35] MEHTA M L, BURKE J. Role of Hydrogen in Stress Corrosion Cracking of Austenitic Stainless Steels[J]. Corrosion, 1975, 31(3): 108-110.
- [36] DOSHIDA T, TAKAI K. Dependence of Hydrogen-Induced Lattice Defects and Hydrogen Embrittlement of Cold-Drawn Pearlitic Steels on Hydrogen Trap State, Temperature, Strain Rate and Hydrogen Content[J]. Acta Materialia, 2014, 79: 93-107.
- [37] XING Xiao, CHENG Ran, CUI Gan, et al. Quantification of the Temperature Threshold of Hydrogen Embrittlement in X90 Pipeline Steel[J]. Materials Science and Engineering: A, 2021, 800: 140118.
- [38] MOMOTANI Y, SHIBATA A, TSUJI N. Hydrogen Embrittlement Behaviors at Different Deformation Temperatures in As-Quenched Low-Carbon Martensitic Steel[J]. International Journal of Hydrogen Energy, 2022, 47(5): 3131-3140.
- [39] GALLIANO F, ANDRIEU E, BLANC C, et al. Effect of Trapping and Temperature on the Hydrogen Embrittlement Susceptibility of Alloy 718[J]. Materials Science and Engineering: A, 2014, 611: 370-382.
- [40] ZHANG Ti-ming, ZHAO Wei-min, ZHAO Yu-jiao, et al. Effects of Surface Oxide Films on Hydrogen Permeation and Susceptibility to Embrittlement of X80 Steel under Hydrogen Atmosphere[J]. International Journal of Hydrogen Energy, 2018, 43(6): 3353-3365.
- [41] AMARO R L, DREXLER E S, SLIFKA A J. Fatigue Crack Growth Modeling of Pipeline Steels in High Pressure Gaseous Hydrogen[J]. International Journal of Fatigue, 2014, 62: 249-257.
- [42] STALHEIM D, BOGGESS T, SAN MARCHI C, et al. Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen[C]//Proceedings of 2010 8th International Pipeline Conference. Calgary: [s. n.], 2011: 529-537.
- [43] SAN MARCHI C, SOMERDAY B P, NIBUR K A, et al. Fracture and Fatigue of Commercial Grade API Pipeline Steels in Gaseous Hydrogen[C]//Proceedings of ASME 2010 Pressure Vessels and Piping Division/K-PVP Conference. Bellevue: [s. n.], 2011.
- [44] SAN MARCHI C, SOMERDAY B P, NIBUR K A, et al. Fracture Resistance and Fatigue Crack Growth of X80 Pipeline Steel in Gaseous Hydrogen[C]//Proceedings of ASME 2011 Pressure Vessels and Piping Conference. Baltimore: [s. n.], 2012.
- [45] SLIFKA A J, DREXLER E S, NANNINGA N E, et al. Fatigue Crack Growth of Two Pipeline Steels in a Pressurized Hydrogen Environment[J]. Corrosion Science, 2014, 78: 313-321.
- [46] ALVARO A, OLDEN V, MACADRE A, et al. Hydrogen Embrittlement Susceptibility of a Weld Simulated X70 Heat Affected Zone under H<sub>2</sub> Pressure[J]. Materials Science and Engineering: A, 2014, 597: 29-36.
- [47] MORO I, BRIOTTET L, LEMOINE P, et al. Hydrogen Embrittlement Susceptibility of a High Strength Steel X80[J]. Materials Science and Engineering: A, 2010, 527(27-28): 7252-7260.
- [48] KUMNICK A J, JOHNSON H H. Hydrogen and Deuterium in Iron, 9-73 °C[J]. Acta Metallurgica, 1977, 25(8): 891-895.
- [49] NANNINGA N E, LEVY Y S, DREXLER E S, et al. Comparison of Hydrogen Embrittlement in Three Pipeline Steels in High Pressure Gaseous Hydrogen Environments[J]. Corrosion Science, 2012, 59: 1-9.
- [50] 张体明. 高压煤制气管线 X80 钢焊接接头的氢致脆化研究[D]. 东营: 中国石油大学(华东), 2016.
- ZHANG Ti-ming. Study on Hydrogen Embrittlement of X80 Pipeline Steel Welded Joints in High Pressure Coal Gas Environment[D]. Dongying: China University of Petroleum (Huadong), 2016.
- [51] NGUYEN T T, PARK J S, KIM W S, et al. Environment Hydrogen Embrittlement of Pipeline Steel X70 under Various Gas Mixture Conditions with in Situ Small Punch Tests[J]. Materials Science and Engineering: A, 2020, 781: 139114.
- [52] AN Teng, PENG Huang-tao, BAI Peng-peng, et al. Influence of Hydrogen Pressure on Fatigue Properties of X80 Pipeline Steel[J]. International Journal of Hydrogen Energy, 2017, 42(23): 15669-15678.
- [53] MENG Bo, GU Chao-hua, ZHANG Lin, et al. Hydrogen Effects on X80 Pipeline Steel in High-Pressure Natural Gas/Hydrogen Mixtures[J]. International Journal of Hydrogen Energy, 2017, 42(11): 7404-7412.
- [54] NGUYEN T T, PARK J, KIM W S, et al. Effect of Low Partial Hydrogen in a Mixture with Methane on the Mechanical Properties of X70 Pipeline Steel[J]. International Journal of Hydrogen Energy, 2020, 45(3): 2368-2381.
- [55] 赵德辉, 徐庆虎, 崔德春, 等. 管线钢在含氢气的煤制天然气中服役安全性评估[J]. 工程科学学报, 2016, 38(7): 952-957.
- ZHAO De-hui, XU Qing-hu, CUI De-chun, et al. Safety Evaluation of Pipeline Steels under SNG Containing H<sub>2</sub>[J]. Chinese Journal of Engineering, 2016, 38(7): 952-957.
- [56] 关鸿鹏, 林振娟, 李瑜仙, 等. X70 管线钢及焊缝在模拟煤制气含氢环境下的氢脆敏感性[J]. 工程科学学报, 2017, 39(4): 535-541.
- GUAN Hong-peng, LIN Zhen-xian, LI Yu-xian, et al. Hydrogen Embrittlement Susceptibility of the X70 Pipeline Steel Substrate and Weld in Simulated Coal Gas

- Containing Hydrogen Environment[J]. Chinese Journal of Engineering, 2017, 39(4): 535-541.
- [57] 史昊, 邢云颖, 王修云. 煤制气环境中氢含量对 X80 管线钢氢脆敏感性的影响规律[J]. 腐蚀与防护, 2018, 39(5): 336-339.
- SHI Hao, XING Yun-ying, WANG Xiu-yun. Influence Law of Hydrogen Content in Coal Gas System on Hydrogen Embrittlement Sensitivity of X80 Pipeline Steel[J]. Corrosion & Protection, 2018, 39(5): 336-339.
- [58] 金立果, 邢云颖. X80 管线钢在含氢煤制气环境中的氢脆敏感性[J]. 腐蚀与防护, 2017, 38(5): 361-364.
- JIN Li-guo, XING Yun-ying. Susceptibility of X80 Pipeline Steel to Hydrogen Embrittlement in Coal Gas Environment Containing Hydrogen[J]. Corrosion & Protection, 2017, 38(5): 361-364.
- [59] TABKHI F, AZZARO-PANTEL C, PIBOULEAU L, et al. A Mathematical Framework for Modelling and Evaluating Natural Gas Pipeline Networks under Hydrogen Injection[J]. International Journal of Hydrogen Energy, 2008, 33(21): 6222-6231.
- [60] HAESELDONCKX D, D'HAESELEER W. The Use of the Natural-Gas Pipeline Infrastructure for Hydrogen Transport in a Changing Market Structure[J]. International Journal of Hydrogen Energy, 2007, 32(10-11): 1381-1386.
- [61] International Energy Agency. Limits on Hydrogen Blending in Natural Gas Networks[EB/OL]. (2020-03-04) [2021-07-13]. <https://www.iea.org/data-and-statistics/charts/limits-on-hydrogen-blending-in-natural-gas-networks-2018>
- [62] ĆWIEK J. Prevention Methods Against Hydrogen Degradation of Steel[J]. Journal of Achievements in Materials and Manufacturing Engineering, 2010, 43(1): 214-221.
- [63] HARDIE D, CHARLES E A, LOPEZ A H. Hydrogen Embrittlement of High Strength Pipeline Steels[J]. Corrosion Science, 2006, 48(12): 4378-4385.
- [64] KOMATSUZAKI Y, JOO H, YAMADA K. Influence of Yield Strength Levels on Crack Growth Mode in Delayed Fracture of Structural Steels[J]. Engineering Fracture Mechanics, 2008, 75(3/4): 551-559.
- [65] CABRINI M, LORENZI S, MARCASSOLI P, et al. Hydrogen Embrittlement Behavior of HSLA Line Pipe Steel under Cathodic Protection[J]. Corrosion Reviews, 2011, 29(5/6): 261-274.
- [66] 刘自亮, 熊思江, 郑津洋, 等. 氢气管道与天然气管道的对比分析[J]. 压力容器, 2020, 37(2): 56-63.
- LIU Zi-liang, XIONG Si-jiang, ZHENG Jin-yang, et al. Comparative Analysis of Hydrogen Pipeline and Natural Gas Pipeline[J]. Pressure Vessel Technology, 2020, 37(2): 56-63.
- [67] ZHAO Wei-min, ZHANG Ti-ming, ZHAO Yu-jiao, et al. Hydrogen Permeation and Embrittlement Susceptibility of X80 Welded Joint under High-Pressure Coal Gas Environment[J]. Corrosion Science, 2016, 111: 84-97.
- [68] STALHEIM D, BOGGESS T, BROMLEY D, et al. Continued Microstructure and Mechanical Property Performance Evaluation of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen[C]//Volume 3: Materials and Joining. Calgary: American Society of Mechanical Engineers, 2012.
- [69] KHATIB ZADEH DAVANI R, MIRESMAEILI R, SOLTANMOHAMMADI M. Effect of Thermomechanical Parameters on Mechanical Properties of Base Metal and Heat Affected Zone of X65 Pipeline Steel Weld in the Presence of Hydrogen[J]. Materials Science and Engineering: A, 2018, 718: 135-146.
- [70] PARK G T, KOH S U, JUNG H G, et al. Effect of Microstructure on the Hydrogen Trapping Efficiency and Hydrogen Induced Cracking of Linepipe Steel[J]. Corrosion Science, 2008, 50(7): 1865-1871.
- [71] CHAN S L I. Hydrogen Trapping Ability of Steels with Different Microstructures[J]. Journal of the Chinese Institute of Engineers, 1999, 22(1): 43-53.
- [72] RAMÍREZ E, GONZÁLEZ-RODRIGUEZ J G, TORRES-ISLAS A, et al. Effect of Microstructure on the Sulphide Stress Cracking Susceptibility of a High Strength Pipeline Steel[J]. Corrosion Science, 2008, 50(12): 3534-3541.
- [73] JEFFREY V, QINGJUN Z, QINGLONG L, et al. The influence of microstructure on the hydrogen embrittlement susceptibility of martensitic advanced high strength steels[J]. Materials Today Communications, 2018, 17: 1-14.
- [74] LI Jing, GAO Xiu-hua, DU Lin-xiu, et al. Relationship between Microstructure and Hydrogen Induced Cracking Behavior in a Low Alloy Pipeline Steel[J]. Journal of Materials Science & Technology, 2017, 33(12): 1504-1512.
- [75] VENEZUELA J, ZHOU Qing-jun, LIU Qing-long, et al. The Influence of Microstructure on the Hydrogen Embrittlement Susceptibility of Martensitic Advanced High Strength Steels[J]. Materials Today Communications, 2018, 17: 1-14.
- [76] TAO Ping, GONG Jian-ming, WANG Yan-fei, et al. Modeling of Hydrogen Diffusion in Duplex Stainless Steel Based on Microstructure Using Finite Element Method[J]. International Journal of Pressure Vessels and Piping, 2020, 180: 104031.
- [77] HE Jun, CHEN Lin, TAO Xuan, et al. Hydrogen Embrittlement Behavior of 13Cr-5Ni-2Mo Supermartensitic Stainless Steel[J]. Corrosion Science, 2020, 176: 109046.
- [78] SAN MARCHI C, SOMERDAY B. Technical reference for hydrogen compatibility of materials[R]. Office of Scientific and Technical Information (OSTI), 2012.
- [79] 张体明, 王勇, 赵卫民, 等. 模拟煤制气环境下 X80 管线钢及 HAZ 的氢脆敏感性[J]. 焊接学报, 2015, 36(9): 43-46.
- ZHANG Ti-ming, WANG Yong, ZHAO Wei-min, et al. Hydrogen Embrittlement Susceptibility of X80 Steel Substrate and HAZ in Simulated Coal Gas Environment[J]. Transactions of the China Welding Institution, 2015, 36(9): 43-46.
- [80] 陈瑞, 郑津洋, 徐平, 等. 金属材料常温高压氢脆研究进展[J]. 太阳能学报, 2008, 29(4): 502-508.
- CHEN Rui, ZHENG Jin-yang, XU Ping, et al. Hydrogen Embrittlement of Metallic Materials in high-Pressure

- Hydrogen at Normal Temperature[J]. *Acta Energiæ Solaris Sinica*, 2008, 29(4): 502-508.
- [81] XUE H B, CHENG Y F. Characterization of Inclusions of X80 Pipeline Steel and Its Correlation with Hydrogen-Induced Cracking[J]. *Corrosion Science*, 2011, 53(4): 1201-1208.
- [82] FINDLEY K O, O'BRIEN M K, NAKO H. Critical Assessment 17: Mechanisms of Hydrogen Induced Cracking in Pipeline Steels[J]. *Materials Science and Technology*, 2015, 31(14): 1673-1680.
- [83] SONG E J, SUH D W, BHADSHIA H K D H. Theory for Hydrogen Desorption in Ferritic Steel[J]. *Computational Materials Science*, 2013, 79: 36-44.
- [84] NOVAK P, YUAN R, SOMERDAY B P, et al. A Statistical, Physical-Based, Micro-Mechanical Model of Hydrogen-Induced Intergranular Fracture in Steel[J]. *Journal of the Mechanics and Physics of Solids*, 2010, 58(2): 206-226.
- [85] CHOO W Y, LEE J Y. Effect of Cold Working on the Hydrogen Trapping Phenomena in Pure Iron[J]. *Metallurgical Transactions A*, 1983, 14(7): 1299-1305.
- [86] CHOO W Y, LEE J Y. Thermal Analysis of Trapped Hydrogen in Pure Iron[J]. *Metallurgical Transactions A*, 1982, 13(1): 135-140.
- [87] WALLAERT E, DEPOVER T, ARAFIN M, et al. Thermal Desorption Spectroscopy Evaluation of the Hydrogen-Trapping Capacity of NbC and NbN Precipitates[J]. *Metallurgical and Materials Transactions A*, 2014, 45(5): 2412-2420.
- [88] DREXLER A, DEPOVER T, VERBEKEN K, et al. Model-Based Interpretation of Thermal Desorption Spectra of Fe-C-Ti Alloys[J]. *Journal of Alloys and Compounds*, 2019, 789: 647-657.
- [89] WEI F G, HARA T, TSUZAKI K. Precise Determination of the Activation Energy for Desorption of Hydrogen in Two Ti-Added Steels by a Single Thermal-Desorption Spectrum[J]. *Metallurgical and Materials Transactions B*, 2004, 35(3): 587-597.
- [90] LEE J L, LEE J Y. The Interaction of Hydrogen with the Interface of  $Al_2O_3$  Particles in Iron[J]. *Metallurgical Transactions A*, 1986, 17(12): 2183-2186.
- [91] SHI Rong-jian, CHEN Lin, WANG Zi-dong, et al. Quantitative Investigation on Deep Hydrogen Trapping in Tempered Martensitic Steel[J]. *Journal of Alloys and Compounds*, 2021, 854: 157218.
- [92] JACK T A, POURAZIZI R, OHAERI E, et al. Investigation of the Hydrogen Induced Cracking Behaviour of API 5L X65 Pipeline Steel[J]. *International Journal of Hydrogen Energy*, 2020, 45(35): 17671-17684.
- [93] HUANG F, LIU J, DENG Z J, et al. Effect of Microstructure and Inclusions on Hydrogen Induced Cracking Susceptibility and Hydrogen Trapping Efficiency of X120 Pipeline Steel[J]. *Materials Science and Engineering: A*, 2010, 527(26): 6997-7001.
- [94] NAKATANI M, FUJIHARA H, SAKIHARA M, et al. Fatigue Crack Growth Acceleration Caused by Irreversible Hydrogen Desorption in High-Strength Steel and Its Mechanical Condition[J]. *Materials Science and Engineering: A*, 2011, 528(25-26): 7729-7738.
- [95] 刘清华, 唐慧文, 斯庭智. 氢陷阱对钢氢脆敏感性的影响[J]. *材料保护*, 2018, 51(11): 127-132.
- LIU Qing-hua, TANG Hui-wen, SI Ting-zhi. Effects of Hydrogen Traps on the Hydrogen Embrittlement Susceptibility of Steel[J]. *Materials Protection*, 2018, 51(11): 127-132.
- [96] CHENG X Y, ZHANG H X. A New Perspective on Hydrogen Diffusion and Hydrogen Embrittlement in Low-Alloy High Strength Steel[J]. *Corrosion Science*, 2020, 174: 108800.
- [97] DONG C F, LIU Z Y, LI X G, et al. Effects of Hydrogen-Charging on the Susceptibility of X100 Pipeline Steel to Hydrogen-Induced Cracking[J]. *International Journal of Hydrogen Energy*, 2009, 34(24): 9879-9884.
- [98] ESCOBAR D P, MIÑAMBRES C, DUPREZ L, et al. Internal and Surface Damage of Multiphase Steels and Pure Iron after Electrochemical Hydrogen Charging[J]. *Corrosion Science*, 2011, 53(10): 3166-3176.
- [99] HEJAZI D, HAQ A J, YAZDIPOUR N, et al. Effect of Manganese Content and Microstructure on the Susceptibility of X70 Pipeline Steel to Hydrogen Cracking[J]. *Materials Science and Engineering: A*, 2012, 551: 40-49.
- [100] DEPOVER T, VAN DEN ECKHOUT E, VERBEKEN K. The Impact of Hydrogen on the Ductility Loss of Bainitic Fe-C Alloys[J]. *Materials Science and Technology*, 2016, 32(15): 1625-1631.
- [101] DOMIZZI G, ANTERI G, OVEJERO-GARCÍA J. Influence of Sulphur Content and Inclusion Distribution on the Hydrogen Induced Blister Cracking in Pressure Vessel and Pipeline Steels[J]. *Corrosion Science*, 2001, 43(2): 325-339.
- [102] LI Long-fei, SONG Bo, CAI Ze-yun, et al. Effect of Vanadium Content on Hydrogen Diffusion Behaviors and Hydrogen Induced Ductility Loss of X80 Pipeline Steel[J]. *Materials Science and Engineering: A*, 2019, 742: 712-721.
- [103] HUANG F, LI X G, LIU J, et al. Effects of Alloying Elements, Microstructure, and Inclusions on Hydrogen Induced Cracking of X120 Pipeline Steel in Wet  $H_2S$  Sour Environment[J]. *Materials and Corrosion*, 2012, 63(1): 59-66.
- [104] HARA T, ASAH I, OGAWA H. Conditions of Hydrogen-Induced Corrosion Occurrence of X65 Grade Line Pipe Steels in Sour Environments[J]. *Corrosion*, 2004, 60(12): 1113-1121.
- [105] 王洪海, 陈俊德, 陈冬, 等. 高强度低合金钢氢脆预防措施[J]. *石油化工设备*, 2018, 47(5): 48-55.
- WANG Hong-hai, CHEN Jun-de, CHEN Dong, et al. Preventive Measures for Hydrogen Embrittlement of High-Strength Low Alloy Steels[J]. *Petro-Chemical Equipment*, 2018, 47(5): 48-55.
- [106] OHAERI E, SZPUNAR J, FAZELI F, et al. Hydrogen Induced Cracking Susceptibility of API 5L X70 Pipeline Steel in Relation to Microstructure and Crystallographic

- Texture Developed after Different Thermomechanical Treatments[J]. *Materials Characterization*, 2018, 145: 142-156.
- [107] OHAERI E, OMALE J, RAHMAN K M M, et al. Effect of Post-Processing Annealing Treatments on Microstructure Development and Hydrogen Embrittlement in API 5L X70 Pipeline Steel[J]. *Materials Characterization*, 2020, 161: 110124.
- [108] 徐政一, 张鹏远, 孟国哲. 金属氢渗透研究综述[J]. *表面技术*, 2019, 48(11): 45-58.  
XU Zheng-yi, ZHANG Peng-yuan, MENG Guo-zhe. Review of Studies on Metal Hydrogen Permeation[J]. *Surface Technology*, 2019, 48(11): 45-58.
- [109] LIU H W, YA-LUNG H, FICALORA P J. The Control of Catalytic Poisoning and Stress Corrosion Cracking[J]. *Engineering Fracture Mechanics*, 1973, 5(2): 281-292.
- [110] JACOBS A J, CHANDLER W T. Inhibition of Hydrogen Environment Embrittlement by  $\text{SO}_2$ [J]. *Scripta Metallurgica*, 1975, 9(7): 767-769.
- [111] DEIMEL P, LEONHARD H, SATTLER E. Characterization of the Influence of High-Pressure Hydrogen Gas on the Ductility of the Steel 15 MnNi 6 3[J]. *International Journal of Hydrogen Energy*, 1993, 18(4): 313-318.
- [112] KUSSMAUL K, DEIMEL P, FISCHER H, et al. Fracture Mechanical Behaviour of the Steel 15 MnNi 6 3 in Argon and in High Pressure Hydrogen Gas with Admixtures of Oxygen[J]. *International Journal of Hydrogen Energy*, 1998, 23(7): 577-582.
- [113] MICHLER T, BOITSOV I E, MALKOV I L, et al. Assessing the Effect of Low Oxygen Concentrations in Gaseous Hydrogen Embrittlement of DIN 1.4301 and 1.1200 Steels at High Gas Pressures[J]. *Corrosion Science*, 2012, 65: 169-177.
- [114] SOMERDAY B P, SOFRONIS P, NIBUR K A, et al. Elucidating the Variables Affecting Accelerated Fatigue Crack Growth of Steels in Hydrogen Gas with Low Oxygen Concentrations[J]. *Acta Materialia*, 2013, 61(16): 6153-6170.
- [115] 李婷婷. CO 抑制高压临氢管线氢致脆化机理的研究[D]. 东营: 中国石油大学(华东), 2018.  
LI Ting-ting. Study on Inhibition Mechanism of CO on Hydrogen Embrittlement of High-Pressure Hydrogen Transport Pipeline[D]. Dongying: China University of Petroleum (Huadong), 2018.
- [116] SHANG Juan, CHEN Wei-feng, ZHENG Jin-yang, et al. Enhanced Hydrogen Embrittlement of Low-Carbon Steel to Natural Gas/Hydrogen Mixtures[J]. *Scripta Materialia*, 2020, 189: 67-71.
- [117] TAKASUGI T, KIMURA A, SUGIMOTO T, et al. The Effects of Partial Pressure and Strain Rate on Water Vapor- and Hydrogen Gas-Induced Embrittlement of  $\text{Co}_3\text{Ti}$  Alloys[J]. *Acta Materialia*, 1997, 45(11): 4765-4773.
- [118] XIONG Mao-xian, ZHENG Shu-qi, QI Ya-meng, et al. Effect of  $\text{H}_2/\text{CO}_2$  Partial Pressure Ratio on the Tensile Properties of X80 Pipeline Steel in the Absence and Presence of Water[J]. *International Journal of Hydrogen Energy*, 2015, 40(35): 11917-11924.
- [119] 林海, 许杰, 范白涛, 等. L80 钢在  $\text{CO}_2/\text{H}_2\text{S}$  腐蚀环境中的力学特性[J]. *表面技术*, 2016, 45(5): 91-96.  
LIN Hai, XU Jie, FAN Bai-tao, et al. Mechanical Properties of L80 Steel in  $\text{CO}_2/\text{H}_2\text{S}$  Environment[J]. *Surface Technology*, 2016, 45(5): 91-96.
- [120] CHATTERJEE S S, ATEYA B G, PICKERING H W. Effect of Electrodeposited Metals on the Permeation of Hydrogen through Iron Membranes[J]. *Metallurgical Transactions A*, 1978, 9(3): 389-395.
- [121] ZAMANZADEH M, ALLAM A, KATO C, et al. Hydrogen Absorption during Electrodeposition and Hydrogen Charging of Sn and Cd Coatings on Iron[J]. *Journal of the Electrochemical Society*, 1982, 129(2): 284-289.
- [122] MICHLER T, NAUMANN J. Coatings to Reduce Hydrogen Environment Embrittlement of 304 Austenitic Stainless Steel[J]. *Surface and Coatings Technology*, 2009, 203(13): 1819-1828.
- [123] JO K R, CHO L, SULISTIYO D H, et al. Effects of Al-Si Coating and Zn Coating on the Hydrogen Uptake and Embrittlement of Ultra-High Strength Press-Hardened Steel[J]. *Surface and Coatings Technology*, 2019, 374: 1108-1119.
- [124] LEVCHUK D, KOCH F, MAIER H, et al. Deuterium Permeation through Eurofer and  $\alpha$ -Alumina Coated Eurofer[J]. *Journal of Nuclear Materials*, 2004, 328(2/3): 103-106.
- [125] FORCEY K S, ROSS D K, WU C H. The Formation of Hydrogen Permeation Barriers on Steels by Aluminizing[J]. *Journal of Nuclear Materials*, 1991, 182: 36-51.
- [126] WANG Ji-peng, LU Zhao-xia, LING Yun-han, et al. Hydrogen Permeation Properties of  $\text{Cr}_x\text{C}_y/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  Composite Coating Derived from Selective Oxidation of a CrC Alloy and Atomic Layer Deposition[J]. *International Journal of Hydrogen Energy*, 2018, 43(45): 21133-21141.
- [127] ZHOU Qing-yun, LING Yun-han, LU Zhao-xia, et al. Characteristics of Hydrogen Plasma Treatment on  $\text{Al}_2\text{O}_3/\text{Cr}_x\text{O}_y/\text{AlmOn}$  Composite Film via Al-Ion-Implantation and Ultra-Low Partial Pressure Oxidation[J]. *Surface and Coatings Technology*, 2020, 395: 125917.
- [128] IZAWA C, WAGNER S, DEUTGES M, et al. Role of Surface Oxide Layers in the Hydrogen Embrittlement of Austenitic Stainless Steels: A TOF-SIMS Study[J]. *Acta Materialia*, 2019, 180: 329-340.
- [129] NAM T H, LEE J H, CHOI S R, et al. Graphene Coating as a Protective Barrier Against Hydrogen Embrittlement[J]. *International Journal of Hydrogen Energy*, 2014, 39(22): 11810-11817.
- [130] KIM Y S, KIM J G. Electroplating of Reduced-Graphene Oxide on Austenitic Stainless Steel to Prevent Hydrogen Embrittlement[J]. *International Journal of Hydrogen Energy*, 2017, 42(44): 27428-27437.