METABK 55(1) 99-102 (2016)
UDC – UDK 669.15.788:621.791.057:621.78.004.64=111

EFFECTS OF HYDROGEN UPON THE PROPERTIES OF THERMO MECHANICAL CONTROLLED PROCESS (TMCP) STEEL

Received – Prispjelo: 2015-02-11
Accepted – Prihvaćeno: 2015-07-20
Review Paper – Pregledni rad

Research into the effects of hydrogen on the mechanical properties of the material is wide-ranging and time-consuming, since there is no single way of predicting cold cracking that would be applicable to all steel grades. Some research on the action of hydrogen in the weld area has focused on the effects of filler materials, welding parameters, the welding environment and welding process upon the hydrogen content of the weld metal and final effect of the hydrogen content upon the properties of the material.

Key words: Steel X70/X80, hydrogen, welding, TMCP, cold crakcs

INTRODUCTION

Steel produced according to the TCMP process is characterized by high impact toughness and improved strength. Its weldability of these steels is good, since the content of carbon (C < 0,12 %) and other alloy elements. This allows lower preheating temperatures or even the complete omission of preheating as an additional processing phase. Weld metal is an aggregate of base and filler material. However, current research has shown that under certain conditions cold cracks may be developed in the weld metal. Since the base material is made using the TMCP process and itself is not susceptible itself to the formation of cold cracks or damage caused by hydrogen, the problem is almost certainly related to the filler material which, without satisfactory properties and chemical composition, this may result in increased hydrogen absorption causing susceptibility to cold cracking within the weld area [1].

Hydrogen within the material may be found in two states: molecular (H_2), as intercrystalline gaseous inclusions under very high pressure, or in atomic state (H or ionized H^+) in the void spaces of crystalline lattice. According to the reference [1], there are several prerequisites that favor the appearance defects caused by hydrogen in welded joints:

1. Sufficient concentration of hydrogen within the material, generally expressed as initially diffused hydrogen concept (H_D or H_0);
2. Sensitive microstructure (ferrite, martensite/austenit, bainite)
3. Stress level in the material, particularly in the form of residual stresses;
4. Temperature range of between 200 °C and 100 °C;
5. Time

Thermodynamic reactions between iron and water result in the release of hydrogen from water. At room temperature, the activation forces for such reactions are quite small, except in case of strong acids rich in hydrogen ions as the contact media in which steel is immersed. The diffusion of hydrogen into the material may occur in two modes: diffusion from the gaseous phase and diffusion from liquid phase [2]. There are several models describing diffusion from the gaseous phase, though they do not provide full explanations of the process, and the details of how hydrogen is diffused into various materials is still the topic of many discussions. However, the following is generally accepted: the adsorption of hydrogen molecules starts on the surface of the metal, and is then, followed by the dissociation of hydrogen molecules into atoms, which after absorption move through the crystal lattice of the metal via the mechanism of diffusion.

$$H_2 \rightarrow 2\,H_{ads} \qquad (1)$$

$$H_{aps} \Leftrightarrow H_{metal} \qquad (2)$$

The entry of hydrogen into the material is established by monitoring dissociation. Actual surfaces are not usually clean so when confirming hydrogen penetration the surface condition, chemical composition and presence of a protective atmosphere should be taken into consideration.

EFFECT OF HYDROGEN INDUCED EMBRITTLEMENT UPON THE MECHANICAL PROPERTIES OF MATERIAL

It is well known that hydrogen dissolved in the crystal lattice of high strength steel may cause brittle structure to form. This hydrogen, in certain concentrations,

---

Tomić, T.; Kožuh, Z.; Garašić, I., Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia; I. Samardžić, Mechanical Engineering Faculty, University of Osijek, Slavonski Brod, Croatia

may cause instant cracking or stress, or delayed cracking may occur at considerably lower temperatures [2]. Hydrogen in iron has very high endothermic solubility. Hydrogen solubility changes proportionally to temperature, as shown in Figure 1. Hydrogen solubility in molten iron above 1 500 °C is approximately 30 ppm, while in solid state it is approximately 8 ppm [3,4]. Figure 1 shows the influence of temperature on hydrogen solubility depending on transformation temperatures ($\delta \rightarrow \gamma$ and $\gamma \rightarrow \alpha$). Cooling rates after welding are very high, and as a consequence of hydrogen penetration, the full desorption of the absorbed hydrogen from the crystal lattice of material into atmosphere is prevented. It should be noted that a hydrogen content of 1 ppm in high strength steels is sufficient cracking to occur [5].

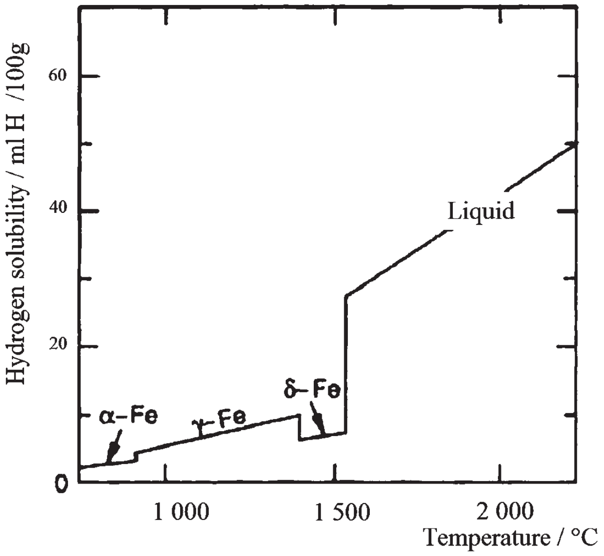

Figure 1 Influence of temperature upon the hydrogen solubility within iron [6]

The level of possible damage to the material depends on the concentration of trapped hydrogen. Hydrogen-induced embrittlement is a type of flaw caused by hydrogen retention between the atoms of the crystal lattice and deformation of the lattice, accompanied by the action of applied or residual stress [6, 7]. This causes limited dislocation movement and due to presence of foreign atoms localized stress resulting in the hardening and embrittlement of the material [7]. The difference in concentration causes the hydrogen to move to deformed, hardened or cold formed areas [8]. Hydrogen concentration is function of the diffusion coefficient. The value of the diffusion coefficient is established experimentaly, and several methods can be used [6]: electrochemical permeation method; sub-surface micro hardness profiling; nuclear reaction analysis; nano-indentation; SSRT (Slow Strain Rate Test) and the glycerin method. Cracks in the material may appear without the presence of external tensile loading if the hydrogen content is over 10 ppm. However, steel grades with yield points higher than 1 000 N/mm^2 are susceptible to the formation of cracking when the hydrogen content is as low as 1 ppm [5]. Figure 2 shows the entry of atomic hydrogen into the micropores of a material where a chemical reaction fusing atomic hydrogen in hydrogen molecules occurs [6].

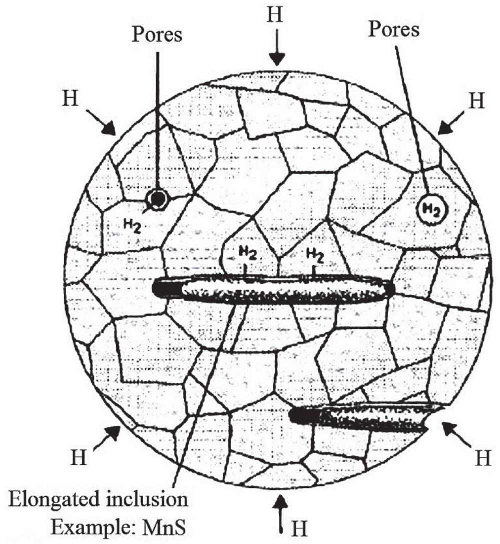

Figure 2 Positioning of molecular hydrogen in micro-pores [6]

The diffusion of hydrogen in the crystal lattices of a metal occurs according to two possible models: the mechanism of substitution diffusion (using vacancies) and the interstitial mechanism. In the substitution mechanism, a leap from one atomic location to another is possible if sufficiently high energy activation is available. The interstitial mechanism is explained by the occurrence of atoms moving from one interstitial space to another. Cold cracking occurs at temperatures below 300 °C and may appear several hours or days after completed welding is completed, causing delayed fracture.

HYDROGEN INFLUENCE ON THE MECHANICAL PROPERTIES OF WELDED JOINTS IN HIGH STRENGTH TMCP STEEL

The influence of hydrogen will be using the example of the API 5L X80 steel grade which is classified as TMPC steel. This steel grade is mainly used to make underground pipelines for the transportation of natural gas, which absorb hydrogen from localized mechanisms of corrosion and cathodic protection. During welding there is a risk of lamellar tearing, the formation of brittle structure and cold cracking [9]. If the material absorbs a certain amount of hydrogen, its impact toughness is reduced and hardening of the steel may occur. Some studies report that a six-fold increase in hydrogen content in the outer pipeline walls has been registered during the first two years of their service life, while this increases to ten-fold over a 15-year period of use [10]. So monitoring hydrogen levels during the service life of these pipes is extremely important. However, levels of hydrogen absorbed during welded should also be accounted for. Generally, cracks formed in the heat affected zone (HAZ) and weld metals of Mn-steels and high strength low alloyed steel are the consequence of diffused hydrogen. Steels with yield points in the range 350 to 600 N/mm^2 have also been monitored. Through research and experiments, it has been established that such cracking basically occurs in non-molten material in HAZ, in single and multipass welds [9]. The formation of such cracks is conditioned by the particular transverse stress state caused by contraction of the material during cooling. In the heat affected zones, these cracks occur less frequently in thinner materials, as they are less rigid and subjected to lower residual stress. A greater danger is represented by cracking in roots of weld metal if the material is more than 30 mm thick [9]. This is generally true of steel with yield point in the range from 355 to 460 N/mm^2. For the steel grades with a yield point over 600 N/mm^2, the critical thickness at which cracking occurs is reduced to between 20 and 25 mm [10]. Cracks in the weld metal developed transversally or longitudinally in relation to the welding direction, while their orientation depends on the presence of hollows and notches and the stress direction [9]. Testing materials for susceptibility to cold cracking is conducted experimentally, using methods specifically developed for this task. The most frequently applied methods are the Tekken and Implant test. Investigation of the formation of cold cracks in TCMP steels (e.g. API 5L X80 steel) indicates cracking spreads from the HAZ area to the weld metal. Analyzing these cracks requires a rather different approach. The rule generally applies that the susceptibility to cracking increases with the strength of the material. However, there is no “critical strength value” for weld metal that would imply the formation of cracks, though some references state that weld metal is more sensitive if its hardness is exceeds the values measured in the HAZ [10]. The chemical composition and mechanical properties of API 5L X80 steel are given in Tables 1, 2.

Table 1 **Chemical composition of X70 and X80 steel grades / wt% [11]**

API 5L	Chemical composition / wt %					
	C	Mn	Si	Nb	Cr	Ni
X70	0,16	1,65	0,45	0,060	0,30	0,30
X80		1,80				
	Mo	P	Al	S	Cu	V
X70	0,35	0,025	0,06	0,015	0,25	0,10
X80						

Table 2 **Mechanical properties of X70 and X80 steel grades [11]**

	Mechanical properties			
	$R_{p0,2}$ / N/mm^2	R_m / N/mm^2	A_5 / %	URL / J at 0°C
X70	485 - 605	575 - 785	>18	>40 - 77
X80	555 - 675	625 - 827	>18	>68 - 120

The TCMP manufacturing process may create three different types of microstructure; ferritic/degenerated pearlitic (F/DP), ferritic/acicular feritic (F/AF), ferritic/bainitic (F/B) [12]. It has been established that certain microstructures tend to trap hydrogen than others, and these are DP, AF, BF and M/A [12, 13]. In the reference [12] acicular ferrite is claimed to be the most desirable microstructure for high strength steels for pipelines, since it provides good resistance to SCC (Sulfide Corrosion Cracking). However, hydrogen diffusion through this microstructure has not yet been fully explained. It is also claimed that bainite may provide higher strength in materials than acicular ferrite, but also could lead to higher susceptibility to hydrogen embrittlement (HE). Nor has a comparison between acicular ferrite and bainite regarding the aspect of hydrogen diffusion has been explained. In the reference [12] it is claimed that residual austenite is an efficient hydrogen trap, since it can be transformed into martensite and then release hydrogen that might be otherwise prove harmful to the product during its service life. Bainitic microstructure and their influence upon hydrogen have also not been fully explained. For example, in [14] it is claimed that bainitic structures are less susceptible to hydrogen induced cracking than ferritic/pearlitic microstructures, due to stress conditions and their homogenous natures. IN fact, bainite may act as a hydrogen trap and absorb higher amounts thus causing brittleness consequently [14]. Most cold cracking is initiated by Mn, Al, Ca and Ti inclusions and may spread transgranularly or intergranularly, depending on cooling regimes. High strength API 5L X80 steel generally containes three types of inclusions, based on Mn, Al and Si. Cold cracks can propagate from all inclusions. The content of diffused hydrogen is also influenced by welding parameters and preheating temperatures. A characteristic feature of the electric arc welding is the occurrence of interactions between the molten material and surrounding atmosphere, which are small in volume and completed in seconds. This process is extremely complex. Gases in the atmosphere separate at different temperatures. Calculating heat input during welding, means including the welding current, arc voltage and welding speed, but not the hydrogen content, contact tip stand-off, gun inclination, type of shielding gas etc.

CONCLUSION

API 5L, X80 steel grade manufactured according the TCMP process has a uniform ferritic/baintitic microstructure. It is resistant to the influence of hydrogen during its service life. It has good weldability, and the welding is possible even without preheating. However, high strength steel is susceptible to hydrogen absorption, even the small amount (1 ppm) that may be introduced during welding. This may be sufficient to trigger generation of cold cracking. It is has also been noted that cold cracking begins in the weld metal rather than in the HAZ. This is due to hydrogen being introduced during welding, along with the hydrogen content of the filler material.

REFERENCES

[1] M. Pitrun, The effect of welding parameters on level of diffusible hydrogen in weld metal deposited using gas shield rutile flux cored wires, Doctoral Thesis, University o Wollongong, Australia (2004)

[2] R.A. Cottis, Hydrogen Embrittlement, in: R.A: Cottis, L.L. Shreir (Eds) Shreir's corrosion, Elsavier, Amsterdam; London (2010), 902-922

[3] D. Seferian, The Metallurgy of Welding, Edition by Građevinska knjiga, Belgrad (1969)

[4] …..: ASME Book, Welding, Brazing and Soldering, Volume 6, USA, (1993)

[5] T. Tomić Kovačević, Influence of hydrogen content on weldability of API 5L X80 steel, Doctoral Thesis, Faculty of mechanical engineering and naval architecture, University of Zagreb (2012)

[6] L. Engel, H. Klingele, Rastermikroskopische Untersuchungen von Metallschaden, Verlag Hanser (1982)

[7] A. Begić Hadžipašić, The influence of microstructure on hydrogen diffusion and embrittlement of multiphase finegrinded steels with increased plasticity and strength, Doctoral Thesis, Faculty of Metallurgy, University of Zagreb, Sisak (2010)

[8] Ø. Grong, Metallurgical Modeling of Welding, London (1997)

[9] P. Nevasmaa, Predictive model for the prevention of weld metal cracking in high strength multipass welds, Academic dissertation, University of Oulu, Finland (2003)

[10] R. Wang, Effects of hydrogen on the fracture toughness of X70 pipeline steel, Corrosion Science 51 (2009), 2803-2810

[11] …API 5L, Specification for pipelines, 42nd Edition, (2000).

[12] G.T. Park, U.S. Koh, H.G. Jung, K.Y. Kim, Effect of microstructure on the hydrogen trapping efficiency and hydrogen induced cracking of line pipe steel, Corrosion Science 50 (2008), 1865-1871

[13] Q. Sha, D. Li, Microstructure, mechanical properties and hydrogen induced cracking susceptibility of X80 pipeline steel with reduced Mn content, Materials Science and Engineering A 585, (2013), 214-221

[14] M.A. Arafin, J.A. Szpunar, Effect of bainitic microstructure on the susceptibility of pipeline steels to hydrogen induced cracking, Materials Science and Engineering A 524 (2011), 4927-4940

Note: Responsible person for English translation is Janet Valentine Berković (MA Oxon)