Effects of Hydrogen Diffusion on the Mechanical Properties of 2.25Cr1Mo0.25V Steel

Jiahao Ge, Changdong Yin, Yiwen Wu and Jianjun Chen*
School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai, China

*Corresponding author email: jjchen@ecust.edu.cn

Abstract. With the rapid development of hydrogen related equipment, how to ensure the reliable operation of these equipment has been an important research topic. 2.25Cr1Mo0.25V steel has high strength, good resistance to hydrogen corrosion and low cost. So it becomes one of most used material for high temperature and high pressure hydrogen systems. In this paper, the glycerine gas gathering experiment, micro hardness test and dynamic tensile experiment were conducted to study the changes of the mechanical properties of 2.25Cr1Mo0.25V steel under varying hydrogen charging time. The relationship between the hydrogen content and material properties were also discussed in detail.

1. Introduction
With the rapid development of new energy technologies, there are high requirements for the strength and ductility of steel equipment serviced in the hydrogen environment. It is well-known that hydrogen will change the metal’s micro-structure and metallography when the hydrogen atom entering steel lattice and induce the embrittlement, cracking or even fracture phenomenon for the facilities, which will have a very serious impact on industrial production and people’s life. Therefore, studying the effect of hydrogen on metal performance has been an important issue for the equipment served in a hydrogen environment[1].

2.25Cr1Mo0.25V steel is chosen as the main material for high-pressure hydrogen system. It is mainly used in the hydrogenation reactors, heat exchangers and oil and gas tanks [2]. These equipment often work in the hydrogen environment and need to check frequently to determine the changes of the mechanical properties after suffering hydrogen damage [3-4]. In this paper the hydrogen content in 2.25Cr1Mo0.25V steel was measured by glycerine gas collection method, and the variation of micro-hardness was obtained after different hydrogen charging time. The tensile experiments were also conducted to obtain the stress and strain curves with different hydrogen charging time. From these tests the effects of hydrogen on the 2.25Cr1Mo0.25V steel were achieved and changes of the mechanical properties such as the elastic modulus and elongation of the material were formulated as a function of the hydrogen content. The graphics of the scanning electron microscope for the cross-section after fracture were analysed and the characteristics and fracture mode of the material were discussed in this paper.

2. Determination of Hydrogen Content
The schematic diagram of the experimental device used in this article is shown in figure 1. In the experimental facility, the anode is connected to a platinum electrode, which loses electrons and an oxidation reaction occurs. The reaction equation is
4OH⁻ → 2H₂O + O₂ ↑ + 4e⁻  \hspace{1cm} (1) 

and the cathode is connected to a sample of metal material with the reaction equation

4H₂O + 4e⁻ → 2H₂ ↑ + 4OH⁻ \hspace{1cm} (2)

During the experiment, the hydrogen charging time were 6, 12, 24, 48 and 72 hours, and the current density was 50mA/cm². The relative position also remains unchanged and only the hydrogen charging time are different.

The diffusion properties of hydrogen in different metals are different, which can be characterized by the diffusion coefficient D. It is well known that the value of the diffusion coefficient changes at the different temperatures, and in this paper the diffusion coefficient will only be studied at the room temperature.

Before hydrogen charging, the specimen’s surface was well polished. After the finish of electrolytic hydrogen charging the specimen’s surface was immediately washed by the ethanol and dried with cold air. Then the specimen was put into a closed glass container. The whole process is within one minute to prevent hydrogen escaping from the specimen. The experimental device is shown in figure 2. The specimen was placed in a glass funnel filled with glycerine and its minimum scale is 0.001ml. After one week it was considered that all the diffusible hydrogen in the specimen had escaped from the specimen due to the low density of hydrogen and insoluble in glycerine. The hydrogen diffused into the funnel and eventually gathers at the top of the funnel. Thus the hydrogen content can be measured directly from reading the scale in the funnel.

The hydrogen content of 2.25Cr1Mo0.25V steel collected by the glycerine gas gathering method is shown in figure 3 for 6, 12, 24, 48 and 72 hours hydrogen charging respectively.

It can be seen from Figure 3, with the increasing of the hydrogen charging time, the hydrogen content diffused from the specimen also increases continuously. When the hydrogen charging time reaches and exceeds 48 hours, the hydrogen content tends to be stable and the final hydrogen content is about 0.095mL.
3. Micro Hardness Analysis

Hardness is the one property of a metal material to resist the object being pressed into the surface of its own. Hardness testing is an important indicator for detecting the mechanical properties of metal materials and is one of the fastest and non-damage testing methods. Hardness units mainly include Brinell hardness (HB), Vickers hardness (HV), Rockwell hardness (HRC), etc. The Vickers hardness measurement began in the 1920s. Compared with other hardness measurement methods, the Vickers hardness measurement is almost independent with the load and the size of the indenter and can reveal the property variation due to the hydrogen charging. Since the outline of the indentation is clear under the microscope lens, the measurement is very convenient which makes it become one of the most widely used hardness measurement methods. The load of micro Vickers hardness is less than 1.961N, and it is very suitable for the hardness measurement for metal foil or very thin surface. The Vickers hardness tester and photograph of indentation under Vickers hardness tester is shown in figure 4.

![Vickers hardness tester and photograph of indentation under Vickers hardness tester.](image)

Because the micro hardness device has high requirements for the smoothness and flatness of the specimen surface, the oxide scale and dirty stuff should be removed before the hardness measurement. The specimen used in this article was cut to a 20×20×1mm cubic and the surface was polished by sandpaper.

The changes of hardness value of 2.25Cr1Mo0.25V steel from surface to interior of the specimen are shown in figures 5.
4. Tensile Test and Morphology of Fracture Section
To study the mechanical properties of 2.25Cr1Mo0.25V steel under different hydrogen charging time, the dynamic hydrogen charging tensile test of the specimen was performed as well. The specimen is charging hydrogen for 6 hours, 12 hours, 24 hours and 48 hours respectively and then increase the tensile load until the specimen is fractured. The current density of hydrogen charging is 50mA/cm² as before, and the stress-strain curve of the specimen was obtained. Furthermore, the changes of the elastic modulus, elongation and hydrogen embrittlement index of the material are obtained. After the tensile test, the fracture morphology is different under different hydrogen charging times. The fracture morphology is helpful to understand the fracture mode of the material. To examine the fracture morphology of the material more clearly a scanning electron microscope was taken to take photos of the fracture section under different hydrogen charging times. The specimen after tensile test is shown in figure 6 and the graphics of the SEM are shown in figure 7.

Figure 5. Changes of hardness of 2.25Cr1Mo0.25V for different hydrogen charging time.
It can be seen from the figure 5 that the hardness of the 2.25Cr1Mo0.25V steel after hydrogen charging is significantly increased near the surface of the specimen where hydrogen entering the material. With the increase of time the hydrogen in the specimen tends to be saturated. When the hydrogen charging time reaches 48 hours, the hardness of the material increases from 242HV to about 285HV along the thickness section.

Figure 6. Test specimens after fracture.
It can be seen from figure 7 that the number of fracture tough dimple of unhydrogenated 2.25Cr1Mo0.25V steel is relatively large. As the hydrogen charging time increases, the number of tough dimples gradually decreases. When the hydrogen time reaches 48 hours, the tough dimple is basically not seen in the fracture surface, and the fracture mechanism is changed from a plastic failure into a brittle failure. This shows that when the material is not charged with hydrogen, the toughness of the material is good. With the progress of the hydrogen charging process, the hydrogen entered the material and make it become brittle. From the fracture morphology, we can qualitatively analyse the embrittlement effect of hydrogen on the material. In order to quantitatively evaluate the embrittlement degree of hydrogen on the material, the tensile tests were performed for different electrolyte hydrogen charging hours and the stress-strain curves are shown in figure 8. The plasticity index can be used to analyse the degree of hydrogen damage. All properties after different hydrogen charging time are listed in table 1. It can be seen that with increasing of hydrogen charging time, the elastic modulus increase gradually and the elongation value appears to decrease. The changing of the yield tress and the ultimate tensile stress are not monotonous and need a further study.

![Fracture Morphology](image)

**Figure 7.** Morphology of fractures under different hydrogen charging times.

**Figure 8.** Stress-strain curves of 2.25Cr1Mo0.25V steel for different hydrogen charging hours.
Table 1. Relationship between hydrogen charging hour and the mechanical properties.

| Specimen Number | Hydrogen charging time (h) | Yield stress (MPa) | Ultimate tensile strength (MPa) | Elastic modulus (GPa) | Elongation percentage (%) |
|-----------------|---------------------------|--------------------|-------------------------------|-----------------------|---------------------------|
| 1               | 0                         | 687.3              | 796.4                         | 210.2                 | 8.83                      |
| 2               | 6                         | 665.4              | 712.2                         | 213.1                 | 8.12                      |
| 3               | 12                        | 658.3              | 694.3                         | 215.5                 | 7.96                      |
| 4               | 24                        | 666.8              | 703.2                         | 216.4                 | 7.54                      |
| 5               | 48                        | 668.7              | 708.8                         | 216.8                 | 7.26                      |

5. Conclusions
In this paper, the mechanical properties of 2.25Cr1Mo0.25V steel under hydrogen charging were studied mainly through the glycerine gas gathering device, hardness experiment and tensile experiment. The following conclusions were obtained:
1) The hydrogen content increased with the increasing of electrolytic hydrogen charging time. When the hydrogen charging time reaches 48 hours, the hydrogen content diffused in the specimen tends to be constant. The hydrogen content of 2.25Cr1Mo0.25V is about 0.095 mL.
2) The hardness of the 2.25Cr1Mo0.25V steel is increased near the hydrogen charging surface after hydrogen charging, and the hardness of the material decreases gradually from the hydrogen charging surface to the interior of the specimen, with the hydrogen charging time increase, the hydrogen in the specimen tends to be saturated. When the hydrogen charging time reaches 48 hours, the hardness of the sample almost does not change any more. The hardness of 2.25Cr1Mo0.25V increases from 242HV to about 285HV.
3) With the increase of the hydrogen charging time, the material elongation of the specimen is continuously decreasing, the elastic modulus is continuously increasing, and the elongation rate of the material specimen is reduced from 8.83% to 7.26% the elastic modulus increased from 210.2 GPa to 216.8 GPa.

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