Research on hydrogen embrittlement sensitivity of hydrogenation reactor material by small punch test

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ABSTRACT

Small punch test is a near-nondestructive sampling of in-service micro-sample testing technology. After more than three decades of development, it has made great progress in obtaining various mechanical properties of materials. The test has a mature research on the yield strength, tensile strength, fracture toughness and ductile-brittle transition temperature. Based on this test method, the hydrogen embrittlement of 3Cr1Mo1/4V, which has been in service for 10 years, was investigated by low-temperature test. The main research work and achievements are as follows:

(1) Obtained the appropriate hydrogen parameters that can make the concentration reach the saturation.

(2) The ductile-brittle transition temperature before and after hydrogen charging of the four kinds of materials were obtained by the small punch test, including the as-received base material, the weld and their de-brittle state, from which we found that both the ductile-brittle transition temperature of the base metal and weld seam were improved after hydrogen charging. And the hydrogen embrittlement and temper embrittlement have synergistic effect.

Key words： Small punch test; Hydrogen charging; Hydrogen embrittlement; Ductile-brittle transition temperature

INTRODUCTION

Hydrogenation reactor is widely used in modern petroleum refining enterprises to improve the quality of the oil. Hydrocracking or hydrotreating need to be carried out under high temperature and high pressure conditions, contacting with hydrogen, hydrogen sulfide and other corrosive substances, which means the hydrogenation reactor steel must have hydrogen corrosion resistant ability to ensure a certain mechanical properties[1]. Most of the materials used in hydrogenation reactor are mainly made of chromium molybdenum. 3Cr1Mo1/4V is a kind of steel with good hydrogen resistance, which is widely used in some equipment of hydrogenation unit. The 3Cr1Mo1/4V steel studied in this project is the only steel used in hydrogenation reactor in China. It is of great value to study the temper embrittlement and hydrogen embrittlement of the steel.

Compared with the traditional methods to study hydrogen embrittlement, the small punch test will provide a new and simple method. Firstly, the small punch test method requires very few test materials, and can even be sampled directly on the surface of the equipment instead of causing damage to them, which doesn't affect the normal operation of the equipment. Besides, the small punch sample can improve the efficiency of hydrogen charging relatively, because the samples were small, multiple samples can be charged at the same time. And because samples are processed into round slices, the contact area with the electrolytic solution is relatively large; The thickness is only 0.5mm, the time of hydrogen diffusion into the heart of sample is greatly reduced, so hydrogen reached saturation time compared with the conventional way will also be greatly reduced.

Scholars at home and abroad have begun to explore it. T. E. Gacía. etc[2] studied the effect of hydrogen embrittlement to the tensile properties of 3 kinds of Cr Mo steel. The experimental results were compared with the regular sample, which shows that SPT can be used to detect the degradation of steel properties caused by hydrogen. Jae-Woo Park[3] studied the hydrogen embrittlement of the high strength steel for automobile by using SPT, and found that the maximum load of the stress displacement curve decreases with the increase of hydrogen charging time, after a certain period of time.

In this paper, we got the best test parameter of electrolytic hydrogen charging, carried out the low temperature small punch test on the specimen before and after hydrogen charging, then analyzed the changes of ductile-brittle transition temperature and the influence of hydrogen embrittlement on it.

TEST MATERIAL

The material of 3Cr1Mo1/4V was used in the sample is the non - surfacing layer and the five layer surfacing layer in the hydrocracking reactor, which has been in service for 10 years. The design temperature and pressure are 17.8MPa and 454C°. Operating temperature and pressure are 14.2MPa and 345C°. The chemical composition is shown in the table 1. The sample of base metal and the weld all include the as-received and de-embrittlement state. So there are 4 kinds of samples.

Table 1: Chemical composition of the material

element	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu
3Cr-1Mo-1/4V	0.15	0.09	0.54	0.006	0.003	3.07	0.998	0.15	0.017	0.082
	Ti	Nb	V	W	Pb	B	Sb	Sn	As	
	0.028	0.043	0.27	0.01	0.01	0.0014	0.0075	0.0078	0.006	

HYDROGEN CHARGING AND DETERMINATION OF PARAMETERS

To study the influence of hydrogen embrittlement on the performance of hydrogenation reactors, it is necessary to ensure that the hydrogen content is consistent with the actual working conditions. The common methods for hydrogen charging include the room temperature gas phase hydrogen charging, high temperature and high pressure hydrogen charging, molten salt electrolysis hydrogen charging and hydrogen charging by electrolysis aqueous solution. The last method is a simple, safe and efficient. In this paper, hydrogen charging by electrolysis aqueous solution is adopted.

Electrolytic Hydrogen Charging Method and Apparatus

The essence of electrolytic hydrogen charging experiment is electrolyzing water. The solution containing acid or alkali, and the platinum plate is used as an anode, the sample is used as the cathode, they are placed in the electrolyte and pass through a certain size of current. Hydrogen is produced on the cathode (sample), and oxygen is produced on the anode (platinum plate). In this experiment, the electrolyte selected is 0.5mol/L H_2SO_4 aqueous solution, and 0.25g/L As_2O_3 is added into the electrolyte as the poisoning agent to prevent hydrogen atoms from forming hydrogen on the surface of the sample, so as to improve the efficiency of hydrogen charging. Figure 1 shows the electrolytic hydrogen charging test device.

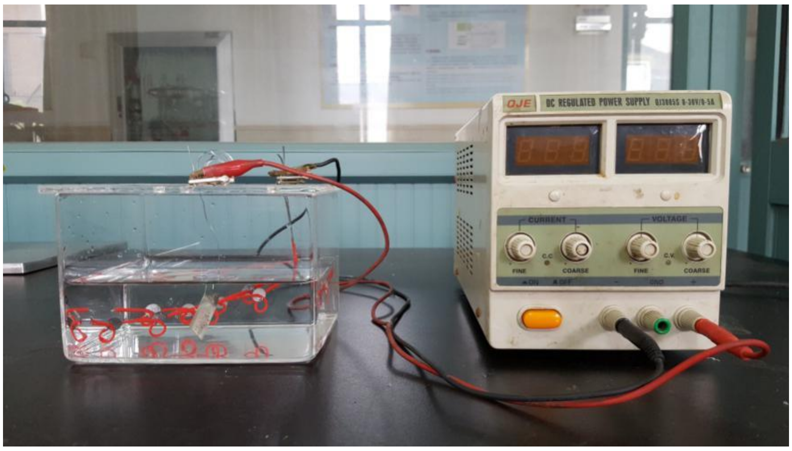

Figure 1 Electrolytic hydrogen charging test device

Determination of Hydrogen Content

Because the sample is small, the hydrogen content is very small even when the hydrogen concentration is high. So a number of samples need to be filled with hydrogen and the gas content should be collected by the same time. In this study, the number of hydrogen filled specimens was 8.

There are several methods for measuring hydrogen concentration: hydrogen permeation method, chemical analysis method, thermal analysis spectrometer and discharge of oil gas collection method. The discharge of oil gas collection method has the advantages of simple structure, low cost and convenient and quick operation. Therefore, it is adopted to determine the content of hydrogen in this paper. Figure 2 shows the device for measuring hydrogen.

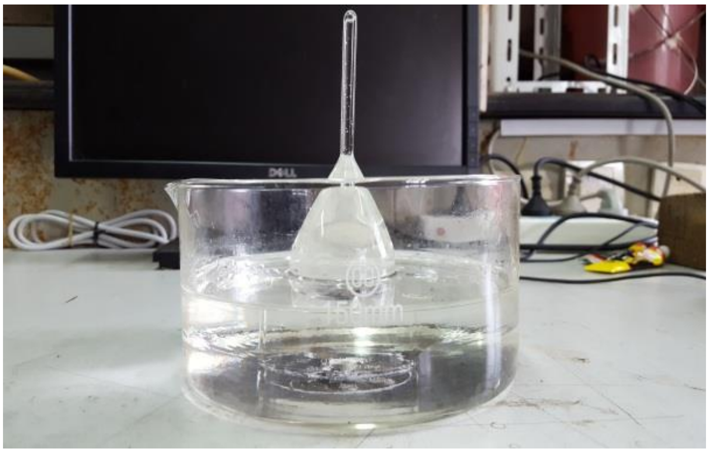

Figure 2 The device for measuring hydrogen

Determination of Hydrogen Charging Parameters

Different hydrogen charging time, charging current and ambient temperature will all affect the hydrogen content. Because the change of the temperature in the hydrogen charging process are small, it is negligible. Therefore, the effect of two factors, including current density and time on hydrogen charging was investigated in this paper.

Figure 3 shows the Relationship of hydrogen charging time and hydrogen concentration. We can see the volume of hydrogen collected from the 8 samples has remained stable since 1h, about 0.04 mL; Figure 4 shows the relationship of hydrogen concentration and current density. The experimental results show that when the current reaches 0.04A, the hydrogen concentration remains unchanged. The hydrogen concentration increased with the increase of hydrogen charging current; when the current size is 0.06A (corresponding to 4.78mA/cm^2), the hydrogen concentration reached 2.33ppm (the maximum). If continue to increase the current density, the hydrogen concentration will show a downward trend. So it is confirmed that the charging parameters should be 0.04A and 1 hour.

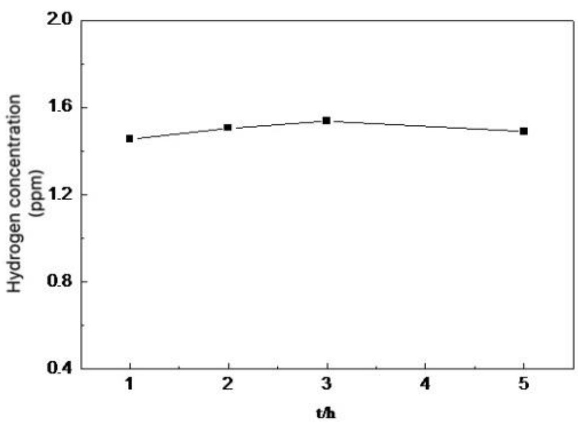

Figure 3 Relationship of charging time and hydrogen concentration

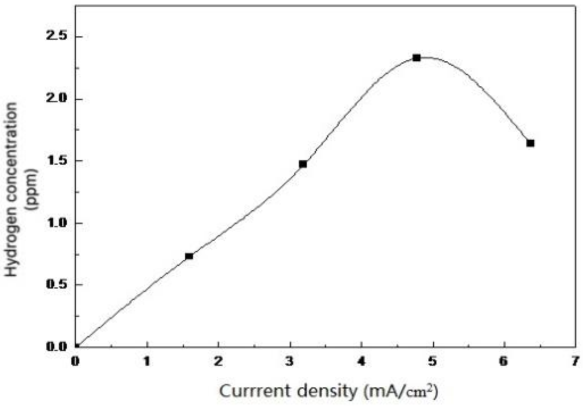

Figure 4 The relationship of hydrogen concentration and current density

STUDY ON THE DUCTILE-BRITTLE TRANSITION TEMPERATURE OF 3Cr1Mo1/4V AFTER HYDROGEN CHARGING

The Ductile-brittle transition Temperature of Small Punch Test

Low temperature small punch test is carried out at different temperatures to gain load displacement curves, integrating the curve can obtain the fracture energy corresponding to each temperature. According to the load displacement curve of the certain temperature (as is shown in figure 5), the area enclosed by the 80% maximum load curve is used as the fracture energy. Then we use Origin to process the data and the Boltzmann function to fit the curve of fracture energy and temperature[5][6][7]. There are four main methods[8] to characterize the T_{SP} (ductile-brittle transition temperature) of small punch. We take the temperature corresponding to the half of the difference between the upper platform and the lower platform on the fitting curve as the T_{SP}; When the fitting curve has no lower platform, then take half of the platform. Figure 6 shows the device for the low temperature SPT.

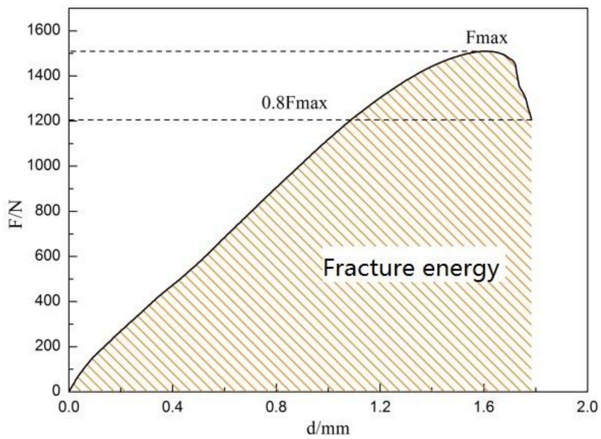

Figure 5 The schematic diagram of the fracture energy

Figure 6 Low temperature SPT device

EXPERIMENTAL RESULTS OF SMALL PUNCH TEST

Experimental Result of The Base Metal

The number of samples is 20~26, 2~3 specimens were tested at the same temperature. According to the load displacement curve, the fracture energy of each specimen is calculated. Curve fitting of experimental results, figure 7(a)~(b) shows the results of T_{SP} of the as-received base metal before hydrogen charging; Figure 7(c)~(d) shows the results of T_{SP} of the de-embrittlement base metal before hydrogen charging; Table 2 shows the T_{SP} and ΔT_{SP} of four states of the base metal

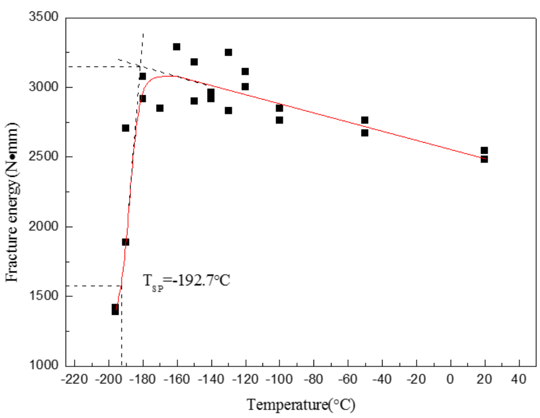

Figure 7 (a)

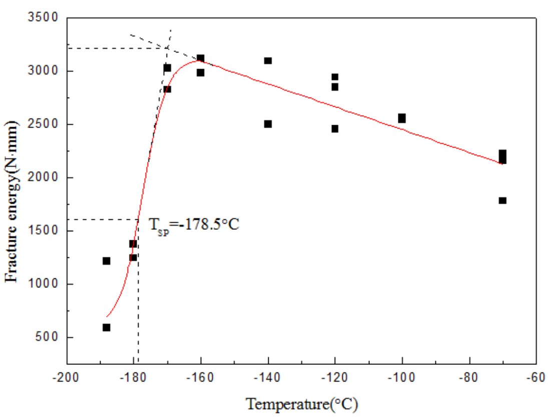

Figure 7 (b)

Figure 7 (a)-(b) The T_{SP} of the as-received base metal before and after hydrogen charging

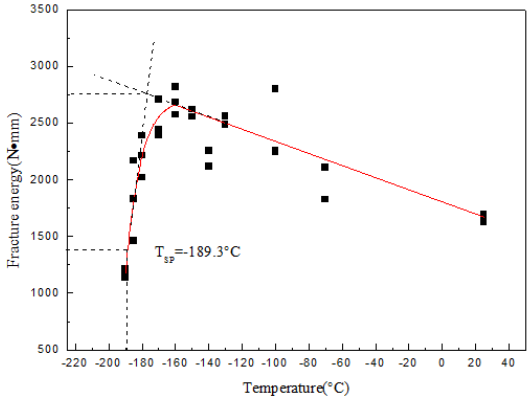

Figure 7 (c)

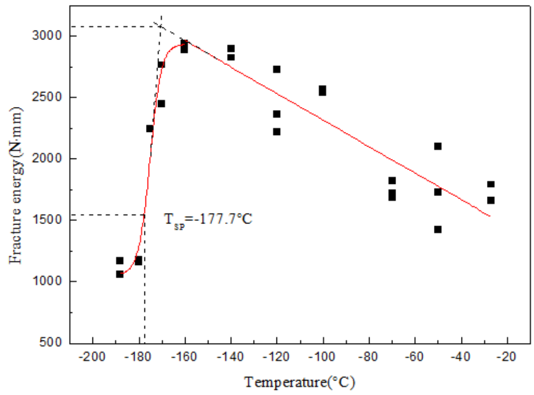

Figure 7 (d)

Figure 7 (c)-(d) The T_{SP} of the de-embrittlement base metal before and after hydrogen charging

Table 2: The T_{SP} and ΔT_{SP} of base metal in different conditions

Type of base metal	Before hydrogen charging	After hydrogen charging	ΔT_{SP}(°C)
As-received	-192.7	-178.5	14.2
De-embrittlement	-189.3	-177.7	11.6
ΔT_{SP}(°C)	-3.4	-0.8	

Experimental Result of The Weld

The experimental process of the weld is similar to the one of the base metal. Curve fitting of experimental results, figure 8 (a)~(b) shows the results of T_{SP} of the as-received weld before and after hydrogen charging; figure 8 (c)~(d) shows the results of T_{SP} of the de-embrittlement weld before and after hydrogen charging; Table 3 shows the T_{SP} and ΔT_{SP} of four states of the weld.

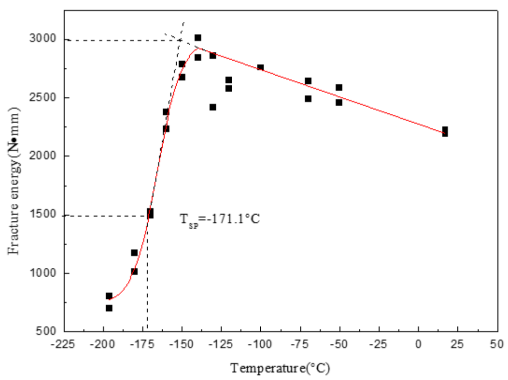

Figure 8 (a)

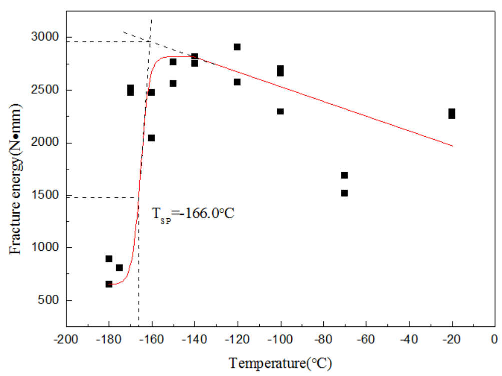

Figure 8 (b)

Figure 8 (a)-(b) The T_{SP} of the as-received weld metal before and after hydrogen charging

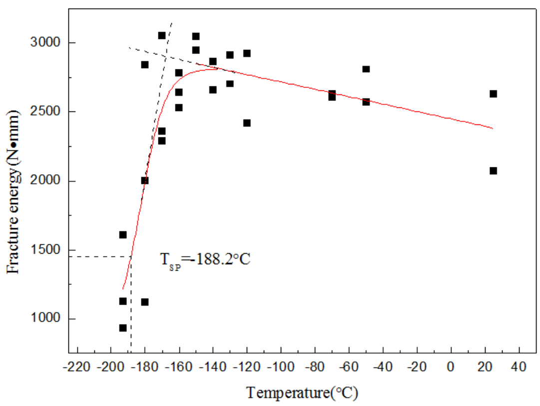

Figure 8 (c)

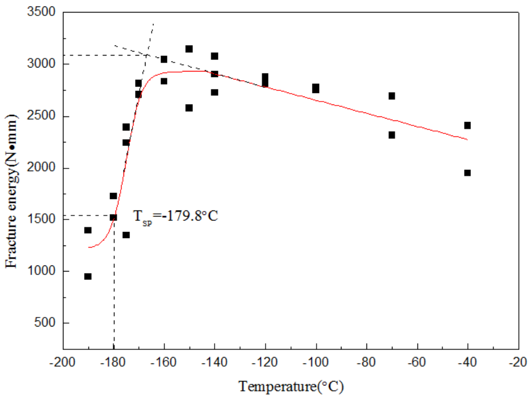

Figure 8 (d)

Figure 8 (c)-(d) The T_{SP} of the de-embrittlement weld metal before and after hydrogen charging

Table 2.2 The T_{SP} and ΔT_{SP} of weld metal in different conditions

Type of weld metal	Before hydrogen charging	After hydrogen charging	ΔT_{SP}(°C)
As-received	-171.1	-166.0	5.1
De-embrittlement	-188.2	-179.8	8.4
ΔT_{SP}(°C)	11.1	13.8	

From the results above we can also see that after ten years in service, there is little temper embrittlement in the base metal of hydrogenation reactor (ΔT_{SP}°C is -3.4; Usually, the T_{sp} of the de-embrittlement would be lower than the one of the as-received one, the unusual result may due to the experimental error, which should be negligible). The weld material had a certain degree of temper embrittlement in the service process (ΔT_{SP}°C is 17.1). The results also show that the T_{SP} of the as-received base metal was increased by 14.2 °C after hydrogen charging, and the one of the de-embrittlement was increased by about 11.6 °C after hydrogen charging. The corresponding weld materials were increased by 5.1°C and 8.4 °C. Hydrogen charging has made the material of the base metal and weld seam a certain degree of brittleness. Based on hydrogen embrittlement, the effect is still able to make the material further embrittlement, the hydrogen embrittlement and temper embrittlement have synergistic effect[9][10][11].

CONCLUSION

In this paper, a small punch test method was used to study the hydrogen charging test of hydrogenation reactor (The material is 3Cr1Mo1/4V), which has been in service for 10 years. The research conclusions of this paper are as follows:

(1) It is confirmed that the hydrogen charging parameters of the following experiments are as follows: the hydrogen charging current is 0.04A and the hydrogen charging time is 1 hours, which can make the hydrogen concentration reach the saturation.

(2) The low temperature small punch test was carried out on four states (the as-

received and de-embrittlement of the base metal and the weld) to obtain the T_{SP}. The hydrogen embrittlement was also measured after hydrogen charging, from which we found that the ductile brittle transition temperature of the base metal and weld seam were both improved. The base metal and weld are all affected by hydrogen embrittlement. The hydrogen embrittlement and temper embrittlement have synergistic effect.

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