An X-ray Study on the Relation Between Hydrogen Embrittlement and Sulphonic Stress Corrosion in High Tension Steel

by Kazuyoshi KAMACHI and Noboru TANI*

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Abstract

It is the object of the present study to clarify the relations with respect to the behavior, between the hydrogen detected by the X-ray line profiles in high tension steels, in the class of 80 kg/mm² charged by cathodic hydrogen, and the hydrogen in the steel immersed in hygrogen sulfide solution.

As the result of the two tests, the following facts were made clear.

(1) In the test made by charging annealed material with cathodic hydrogen, the crystals were deformed plastically, and the lattice of the crystals expanded. In the case of quenched and tempered material, and also in the case of the so-called "received" material, the behavior of hydrogen detected by the X-ray line profiles were mostly static.

(2) In the test made of annealed material in hydrogen sulfide solution, (immersed in the solution non-stressed or restricted by bending stress), there was little change in the X-ray line profiles though the test was continued until cracks due to stress corrosion began to be observed. This was also the case with the "received" material.

The following conclusion can be made from the two tests mentioned above: that the hydrogen in the test (1) behaves differently from that in the test (2), and therefore it is considered that hydrogen is not allowed to invade the lattice of the crystals through the hydrogen sulfide solution.

Introduction

Generally, high tension steels have some problems caused by their high tensile strength and their low absorbed energy. Especially, the sulfide stress corrosion cracking and the delayed fracture of high tension steels are big problems connected with the fracture of constructions. They are both discussed in terms of the hydrogen in steels.[1)]

In this study, the high tension steels were charged cathodically with hydrogen and then examined using the X-ray diffractometer to clarify the phenomenon in the steels. The absorption in hydrogen sulfide solution was also examined, and the relation between sulfide stress corrosion cracking and hydrogen charging was investigated.

Experimental Procedure

Material The material tested was high tension steel of the class 80 kg/mm²

* Department of Industrial Mechanical Engineering

Table 1. Chemical composition (wt%) and mechanical properties of H. T. 80.

Chemical composition

C	Si	Mn	P	S	Ni	Cr	Mo	Cu
0.17	0.15	0.01	0.018	0.018	0.88	0.42	0.47	0.24

Mechanical properties

Yield Strength (kg/mm^2)	Tensile Strength (kg/mm^2)	Elongation (%)
75.7	83.6	26.8

(H. T. 80). The chemical composition and mechanical properties are given in Table 1.

Specimen The specimens used for the cathodic hydrogen charging test were made as follows: A plate of 10 mm thick of H. T. 80 was cut at right angles to the surface of the plate by a metal saw, and the surface cut by the metal saw was ground a surface grinder. The dimensions of the specimen are 35 mm × 9.5 mm × 2 mm. Note that the length of the specimen was parallel to the rolled direction of the plate.

The specimens for the test in hydrogen sulfide solution were made the same as mentioned above, and their dimensions were 120 mm × 9.5 mm × 2 mm. Before the tests each specimen was polished with emery paper of #500, the oil removed, and then polished electrolytically to have a constant surface condition. The composition of the electrolyte was phosphoric acid and chromium trioxide in the ratio 5 : 1 by weight.

Because of the complex mechanical hysterisis of the shaped specimens, three types of heat treatment were performed as follows.

(1) Annealing in vacuum for 1 hour at 1100°C and cooling at the rate of 200°C an hour.

(2) Water quenching after keeping in vacuum for 1 hour at 900°C and tempering for 2 hour at 500°C.

(3) No heat treatment (as received matreial).

Three types of specimens were prepared for this test.

Hydrogen absorption Hydrogen was absorbed in metals by the cathodic electrolytical method. 0.1 N sulfuric acid was used as the electrolyte and 500 mg/l of arsenic trioxide was added to accelerate the hydrogen absorption. The current density was 0.2 A/cm^2, and a platinum rod was used as the anode.

An aerated corrosive medium was used in the test for the sulfide stress corrosion cracking. Hydrogen sulfide gas was generated by the reaction of ferrous sulfide and dilute sulfuric acid, and then dissolved in 0.5% acetic acid solution which is typical corrosive medium used in the test for the sulfide

stress corrosion cracking in high tension steels.[1] The concentration of hydrogen sulfide was from 1000 to 1500 ppm. It was measured by reacting a fixed quantity of hydrogen sulfide solution with excess 0.1 N arsenic trioxide solution, and after filtering, it was titrated with 0.1 N iodide solution.

Specimens were loaded by means of the loading holder as shown in Fig. 1. Each support was made of a glass rod to protect the Galvanic effect, and the distance between the supports was 100 mm. The maximum surface stress was calculated by the degree of the deflection at the middle of the supports. These experiments were performed at room temperature.

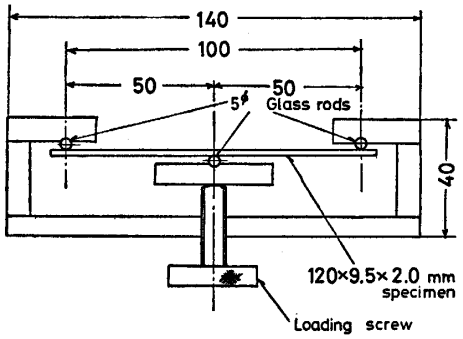


Fig. 1. The shape of the loading holder in the hydrogen sulfide solution. (mm)

X-ray condition Every specimen was washed and dried after the hydrogen charge or after it was immersed in hydrogen sulfide solution at fixed intervals of time, and then the X-ray diffraction profiles (line profiles) were recorded automatically. CrK_α radiation was mainly used, and the voltage of the X-ray tube was 30 Kvp, and the current was 10 mA. The scanning speed of the goniometer was 1/4 deg/min in 2θ, and the chart speed was 600 mm/hr. The observed diffracted plane from the specimen was (211) plane which diffracted the highest order in all planes. The value of the half peak width and peak shift were measured from line profiles. Furthemore to investigate the behavior of the materials in the process of hydrogen absorption, the line profiles were analyzed using the single plane method. The calculated Fourier coefficient Fr was plotted against it's order number n. In other words Fr-n curves were plotted. The relation between $-ln\ Fr/n$ and n may be written as follows.[2]

$$-lnFr/n \simeq 1/N_3 + (1/2N_3^2 + 2\pi^2 l_0^2 \bar{e}^2)n$$

Where N_3a_3 indicates the particle size in crystal if one side of a cell is a_3 in the transformed co-ordinate, and $\bar{e}^2$ is the mean square lattice strain, which means the microscopic strain in the coherent region of the crystal. When $-ln\ Fr/n$ is plotted against n, the above equation indicates a straight line where n is of a low order. The value where the straight line intersects the $-ln\ Fr/n$ axis indicates the value in inverse ratio to the particle size, and the tangent of

the line corresponds to the value of the lattice strain.

Using the above equation, the value of the particle size and lattice strain were determined, and the change in line profiles were observed.

Result and Discussion

In the material as received, the internal stress was large, so that the X–ray line profile was very broad in consquence (more than 1.4° in half peak width), and it was difficult to measure the change of line profiles influenced by hydrogen absorption, so the specimens were annealed. The internal stress in the specimen must be relieved as far as possible by annealing, so that the change in the line profiles may be investigated against the annealing temperature. The results are shown in Fig. 2. The values of half peak width are plotted against the annealing temperature. The measured values of the half peak width decrease with the increase of the annealing temperature, and hold an almost constant

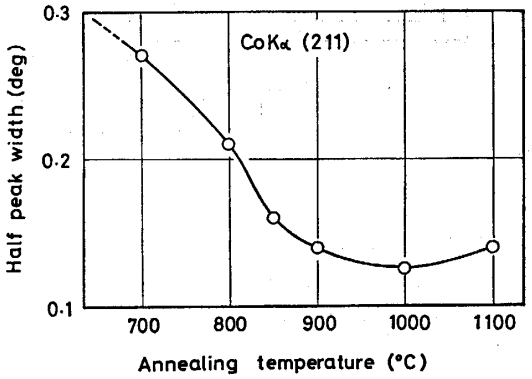


Fig. 2. Half peak width against the temperature of annealing on the condition of 1 hr holding and cooling at the rate of 200°C/hr.

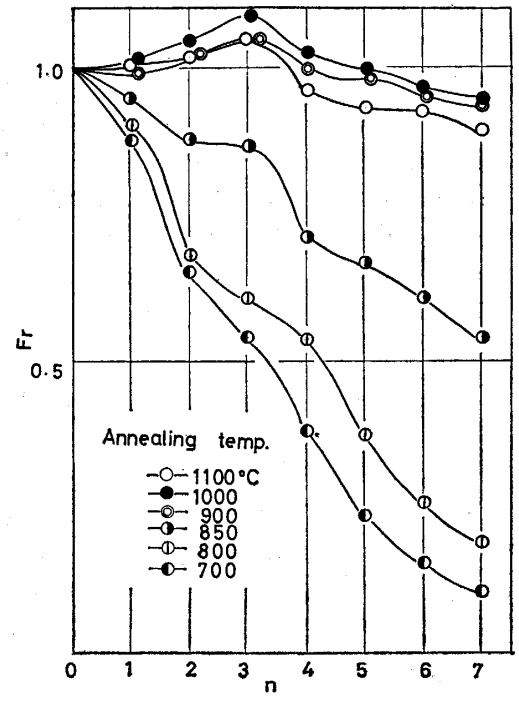


Fig. 3. F_r *vs.* n curves in the process of annealing.

value over 900°C. According to these results, it may be concluded that the residual stress was relieved by the conditions of annealing at 900°C for 1 hour. Further, the profiles were Fourier analyzed to investigate the physical meaning. When the stress remained in the crystal, Fourier coefficient *Fr* decrease of *n* in *Fr–n* curves, and this decrease of *Fr* went down with increase of the annealing temperature, and over the temperature of 900°C the change stopped as shown in Fig. 3. The lattice strain and particle size could be suggested from the plot of $-ln\ Fr/n$ versus *n* curves, and it was therefore recognized that the lattice strain decreases and the particle size increase with increase of the annealing temperature, as shown in Fig. 4.

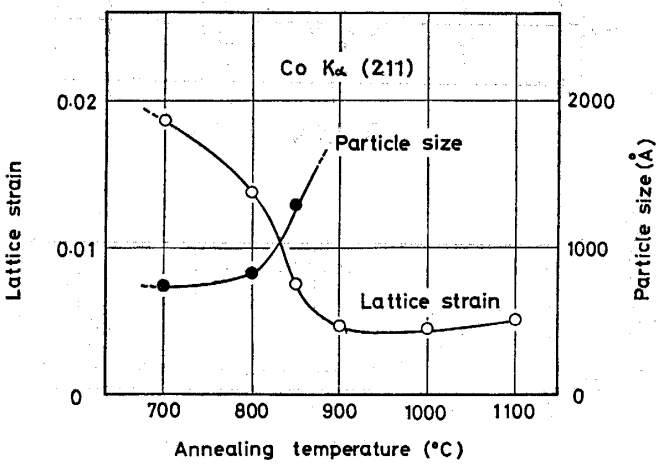


Fig. 4. Lattice strain and particle size against annealing temperature on the condition of 1 hr holding and colling at the rate of 200°C/hr.

Cathodic hydrogen charging test It has been known that steels were deformed plastically by hydrogen, when the hydrogen is charged cathodically into steels.[3] In the case of high tension steel, Fig. 5,6 were obtained by means of the above mentioned test. Considering the state of the specimen deduced by these figures, the value at half peak width was 0.45° in the virgin state, and the ratio at half peak width increased from 1.0 to 1.6 by means of the hydrogen charging. But this broading of the line profile does not change aged at room temperature. These facts clearly indicate that the plastic deformation occured in the crystal. Considering the change of peak position during hydrogen charging, the peak position of the $K\alpha_1$ line shifted 0.35° to a lower angle, and this means that the lattice would be expanded by means of the hydrogen charging. The values of the half peak width of the quenched and tempered material was 1.9° and that of the material as received was 1.4° in the initial state, and the ratio of half peak width did not change greatly in spite of the increasing of hydrogen charging time. Fig. 7～11 were obtained by means of the analysis of X–ray line profiles. According to these figures, it was clear, in the case of the annealed material, that the lattice strain increased and the particle size decreased with the increase of the charging time, and that the lattice strain

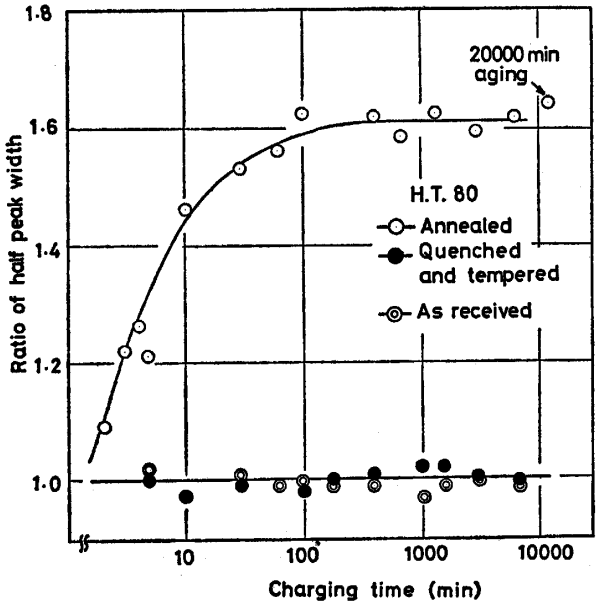


Fig. 5. Ratio of half peak width against cathodic hydrogen charging time, taken from Cr target (211).

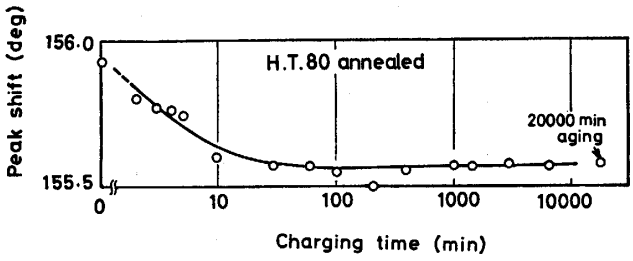


Fig. 6. Peak shift against cathodic hydrogen charging time taken from (211), using CrK_α radiation.

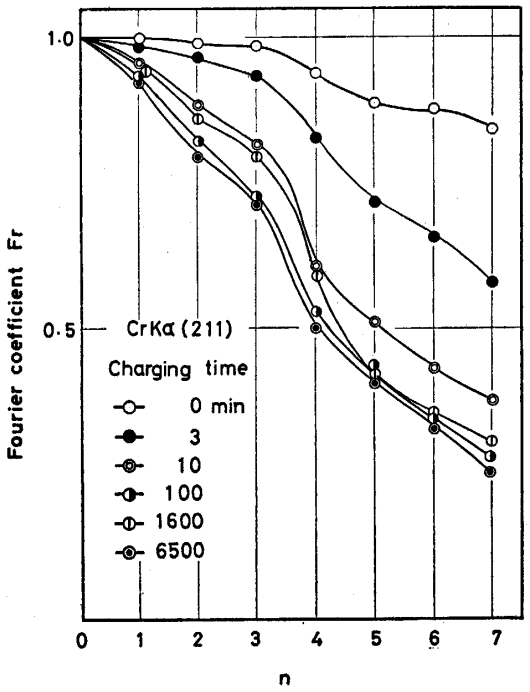


Fig. 7. Fourier coefficient F_r *vs.* n curves in H.T. 80 annealed.

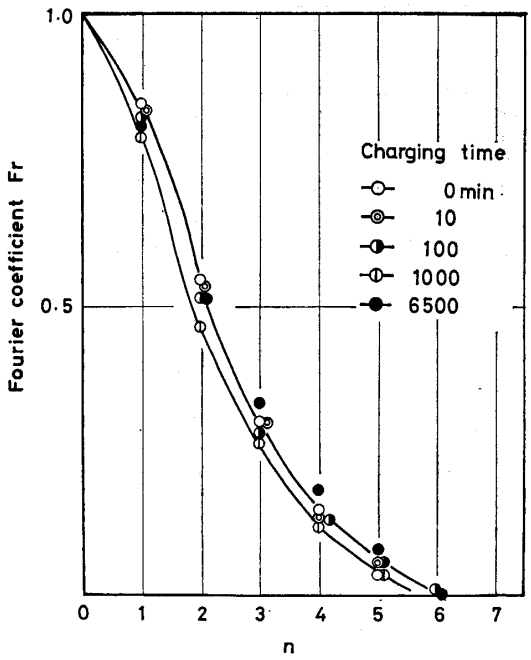


Fig. 8. Fourier coefficient F_r *vs.* n curves. (H.T.80 quenched and tempered)

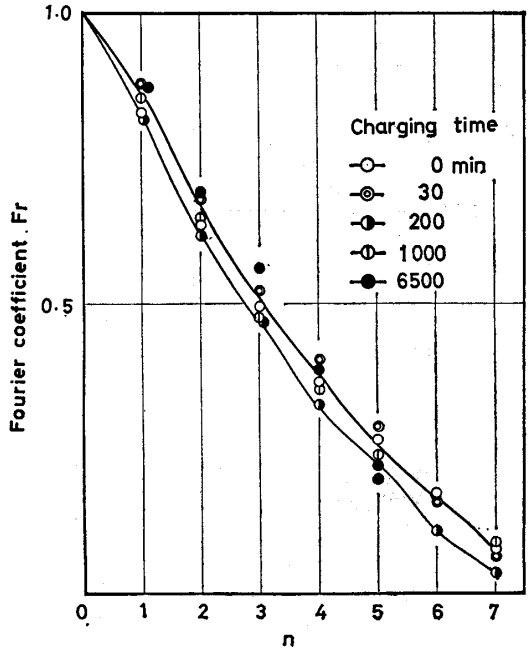


Fig. 9. Fourier coefficient F_r *vs.* n curves. (H.T.80 as received)

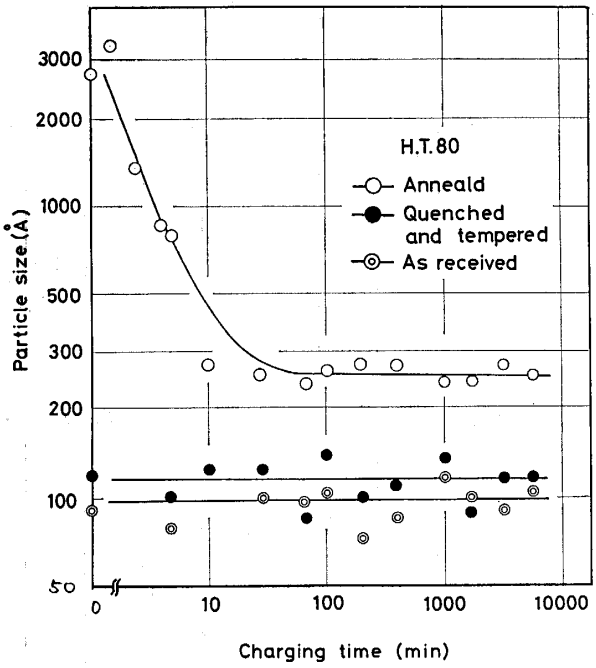


Fig. 10 Particle size against cathodic hydrogen charging time, taken from (211) using CrK_α radiation.

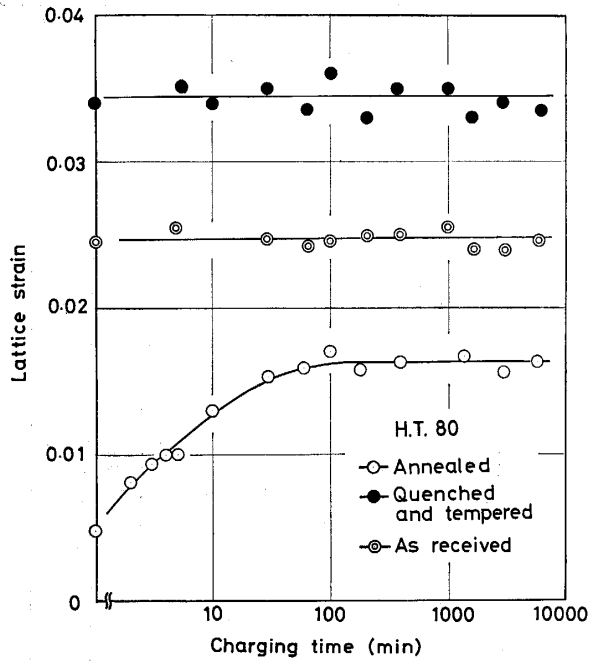


Fig. 11. Lattice strain against cthodic hydrogen charging time, taken from (211) using CrK_α radiation.

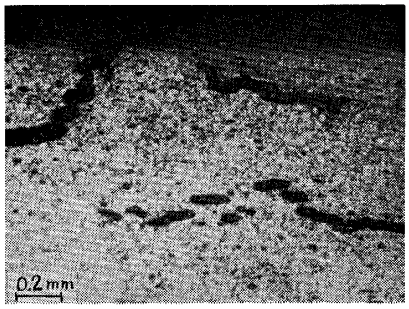


Fig. 12. The blisters in H.T. 80, as received by cathodic hydrogen charging. (3000 min)

saturated within 100 minutes charging with the condition of the current density 0.2 A/cm^2 at room temperature.

It has been reported that normal mild steels are saturated with hydrogen only after more than 5 hours[3], but with high tension steel the permeability of hydrogen is a large value[4]. Therefore it is natural that the saturating time for high tension steel is lower than for mild steels. In the case of the quenched and tempered material and the received material, the line profiles were broad with the level of dozens percent of strain, so that the effect of the hydrogen charging was not remarkable. The value of the lattice strain increased in the annealed material, the received material, and the quenched and tempered material, in that order. It was reported that the lattice was deformed by an amount equivalent to 5% of the strain in tension if the specimen was charged with hydrogen until saturated[5]. So it may be reasonable that there was no clealy change in the quenched and tempered materials, and the received materials due to hydrogen charging. But however, blisters were observed in the metal caused by hydrogen charging. So it may be stable in terms of the energy level to precipitate hydrogen somewhere and to make voids or blisters rather than to let it exist in the lattice for the materials whose internal lattice strain is large. But this point must be discussed further and examined by other methods.

Hydrogen sulfide cracking test The annealed material was immersed, with no load in hydrogen sulfide solution to observe the changes which occure on high tension steel, or the specimen was loaded so as not to deform plastically, but no change in the ratio of half width could be detected as shown in Fig. 14. This behavior in the crystal was compared with the case of Fig. 5. The line plofiles were analyzed, but no change of the lattice strain could be detected clealy, though the observation was continued till a number of cracks were recognized. When the received material was loaded with 70 kg/mm^2 and immersed in the corrosive solution, it was fractured in 2470 minutes. In spite of increasing the immersing time, no change in the ratio of half peak width was detected, as shown in Fig. 17. The X–ray line plofiles were analyzed, but no change of the lattice strain and particle size were detected clearly, either, as shown in Fig. 18 and 19. Many corrosion cracks were observed at right angles to the surface of the plate in tension side by means of the optical microscope. This is shown in Fig. 20.

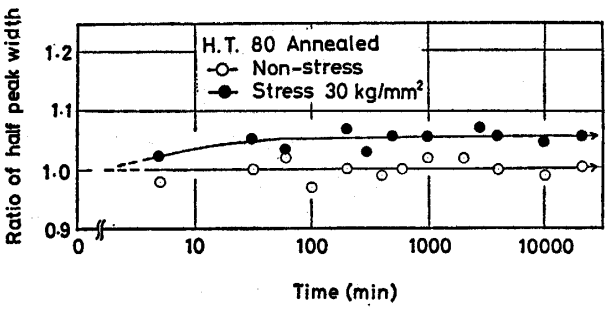


Fig. 13. Ratio of half peak width against testing time in hydrogen sulfide solution, taken from (211) using CrK_α radiation. (Annealed)

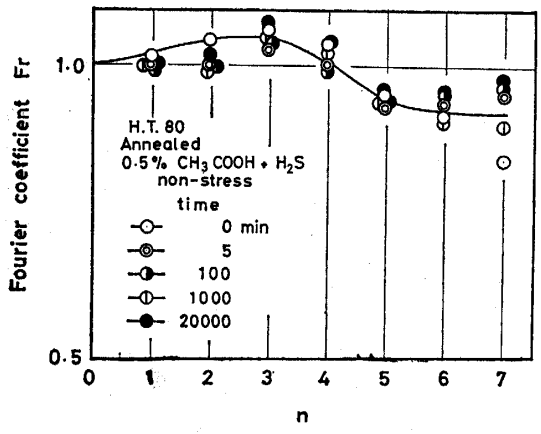


Fig. 14. Fourier coefficient F_r *vs.* n curvs.

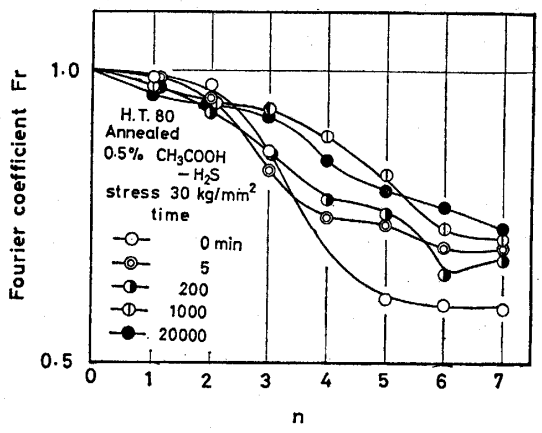


Fig. 15. Fourier coefficient F_r *vs.* n curvs.

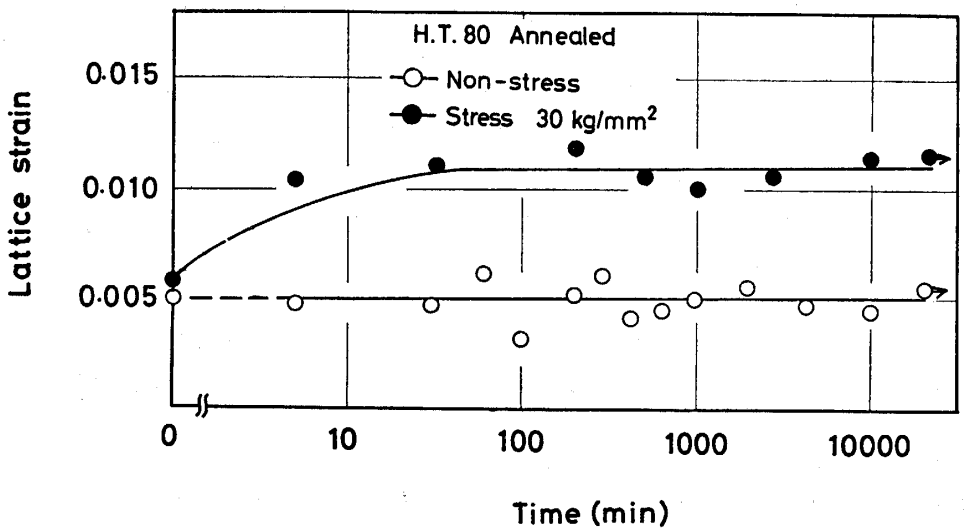


Fig. 16. Lattice strain against testing time in hydrogen sulfide solution, taken from (211) using CrK_α radiation.

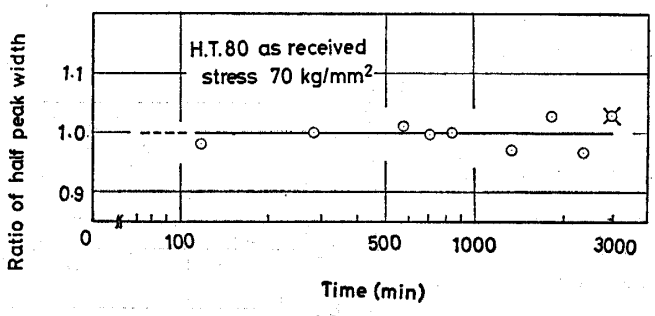


Fig. 17. Ratio of half peak width against testing time in hydrogen sulfide solution under stress 70 Kg/mm² taken from Cr target, (211). (as received)

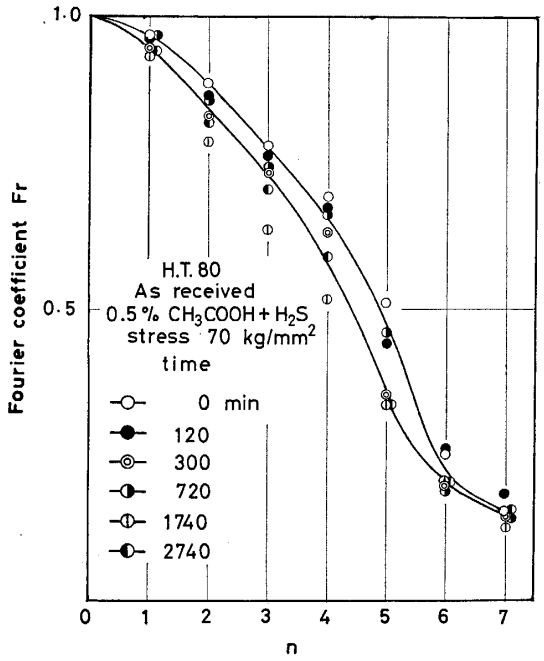


Fig. 18. Fourier coefficient F_r *vs.* n curves. (As received)

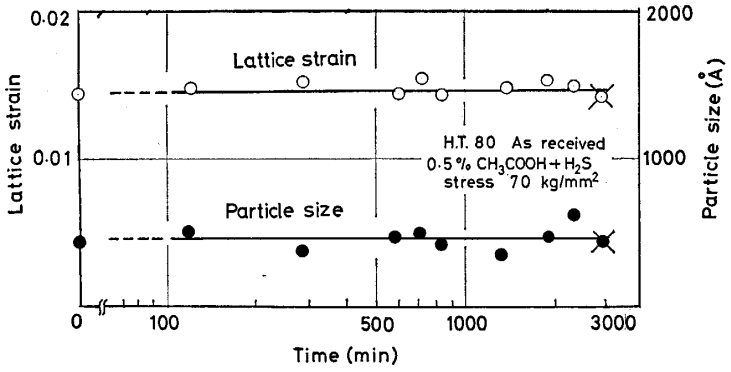
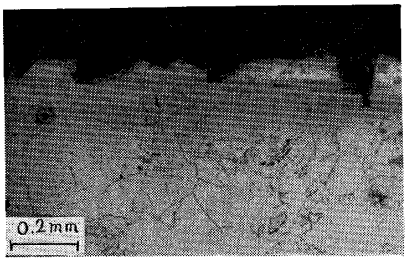
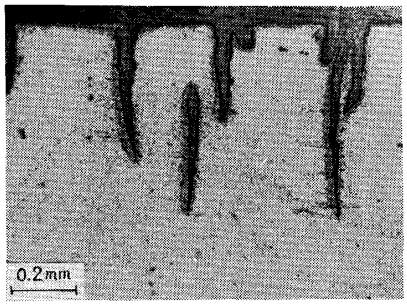


Fig. 19. Lattice strain and particle size against testing time in hydrogen sulfide solution, taken from Cr target, (211) in H.T.80 as received.



(a) H.T.80 annealed, under stress 30 Kg/mm², after 20000 min immersed.



(b) H.T. 80 as received, under stress 30 Kg/mm², after 20000 min immersed.

Fig. 20. The corrosion crackings observed on the tension side of specimen in hydrogen sulfide solution test.
(a) is annealed and (b) is as received.

The change during the test of the cathodic hydrogen charging was compared and discussed with the change during the test immersed in the hydrogen sulfide solution. As the results, it is observed that the behaviors of hydrogen and the change brought about by hydrogen in the steel are completely different in both tests. Therefor, it could be considered that the hydrogen is not allowed to invade the lattice of the crystals through hydrogen sulfide solution. From the viewpoint of the X–ray method, it is obvious that the sulfide stress corrosion cracking in high tension steel depended on diffrent mechanism of the hydrogen embrittlement.

Conclusion

The results of this paper are as follows

(1) The material of which shape is 35 mm × 9.5 mm × 2 mm at length was annealed at 900°C for 1 hour, and thus, the internal stress of this material was relieved.

(2) It is clear that the crystals were deformed plastically and the lattice was expanded on the annealed materials by means of the cathodic hydrogen charging. The quenched and tempered material and the received material therefore showed no clear influence due to the hydrogen, because of the large residual stress within the materials at the initial state.

(3) The materials after annealing were immersed in the hydrogen sulfide solution with no load, or loaded with bending stress. The effect detected by the X–ray line profiles is that the materials show no striking change. Similar results were also obtained with the received material, untill the stress corrosion cracks were observed.

(4) It may be concluded that the hydrogen is not allowed to invade the lattice of the crystal through the hydrogen sulfide solution.

Reference

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