Delayed Fracture Characteristics of Low Alloy Steel in Aqueous Environments*

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Synopsis

The delayed fracture characteristics in various aqueous environments were investigated for two kinds of low alloy high strength steels having sorbitic and martensitic structures, the tensile strength of which were about 125 kg/mm² and 150 kg/mm², respectively. These steels do not fail in the atmosphere under sustained load if the applied stress is not high enough as just below the static bending strength. But the delayed fracture strength of the steel decreases in contact with water, NaCl solution, HCl solution, and acetic acid solution containing H₂S. The results of the observation of the fracture surfaces, crack initiation behaviour in delayed fracture, and quantitative analysis of hydrogen in steel lead the conclusion that the delayed fracture in these environments occurs by hydrogen induced from the surroundings, with the exception of the case that the testing period is extremely prolonged and the decrease of the cross sectional area from corrosion plays an important role.

The dependence of the delayed fracture strength in 0.1 N HCl solution for several low alloy steels on the tempering temperature was investigated. The delayed fracture strength decreases depending mainly on the increase in the hardness above V.H.N. 350. But the peak of the delayed fracture strength is obtained for the steel tempered at 200° to 300°C and an abnormal depression for the steel tempered at about 350°C. For the steel containing much amount of silicon, the peak of the delayed fracture strength shifts to the higher tempering temperature. A similar feature was obtained in the variation of the degree of hydrogen embrittlement with tempering of the steel dipped in 0.1 N HCl solution.

The result of the observation of the metal structure suggests that the variation of delayed fracture strength with tempering is related to the precipitation of carbides at the prior austenitic grain boundaries.

I. Introduction

It is known that the delayed fracture occurs even in the atmosphere when the strength level of the steel is high enough, and this phenomenon has attracted special attentions in developing high strength steels in recent years. Joint bolts, tie rods, and other steel products for a civil engineering use suffer high sustained loads and often aqueous environments such as rain or dew, and the problem of the delayed fracture retards the application of high strength steels for such uses.

As the mechanism of the delayed fracture in corrosive environments, there are two types of proposed

mechanisms; the stress corrosion cracking and the hydrogen cracking where the anodic reaction and the cathodic reaction play main roles, respectively. It is important to know the mechanism of the fracture in actual environments to prevent the fracture of steel products in practical uses, and there are several papers concerning with the mechanisms of the delayed fracture in some experimental environments for martensitic steels.¹⁾⁻⁴⁾

To develop the low alloy high strength steels suitable for steel products under high sustained loads such as high tension bolts and tie rods, the authors investigated the delayed fracture characteristics of steels in the atmosphere or water as usually exposed environments and in NaCl solution, HCl solution, or acetic acid solution saturated with H₂S as promoting environments, furthermore, the changes of the delayed fracture characteristics in these environments accompanied with tempering of hardened steel, because these low alloy steels are usually used in the hardened and tempered condition, and the influence of microstructures on the delayed fracture was discussed.

II. Experimental Procedure

Steels used in this investigation were commercially melted in a basic electric furnace and their chemical compositions are shown in Table 1. They were cast as 1-t ingot and hot rolled to the rods from 8 to 10 mm in diameter. Test pieces were machined from the rods after hardening and tempering.

For the delayed fracture test, notched cylindrical test pieces shown in Fig. 1 were used. The static bending strength of the steel was determined previously with an increasing load in the atmosphere for a similar test piece to those used in the delayed fracture tests, and then applied loads were decided. The bending moment was applied by the dead weight sustained at an extended end of the test piece in a cantilever type

Table 1. Chemical compositions of steels used

Steel	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Others
A	0.20	0.27	0.68	0.018	0.019	0.13	0.05	1.00	—	—
B	0.21	0.75	1.34	0.013	0.009	0.16	0.14	1.67	—	Ti 0.13
C	0.39	0.27	0.74	0.015	0.017	0.15	0.06	1.01	—	—
D	0.37	0.27	0.73	0.019	0.014	0.14	0.10	1.01	0.19	—
D-1	0.36	0.25	0.66	0.021	0.013	0.20	0.10	0.98	0.19	—
M	0.36	0.64	0.82	0.015	0.008	0.10	0.04	1.38	0.59	V 0.15

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Fig. 1. Test specimen for delayed fracture test (mm)

testing machine. The test solution was dropped at the notched part of the test piece with the feeding speed from 4 to 6 drops per minute at room temperature, and the time from the beginning of dropping solution to fracture was measured. Applied moments were expressed as elastic stresses for convenience.

III. Results and Discussion

1. Influence of Environments

The results of delayed fracture test in various environments are shown in Fig. 2 for steel *B* of which tensile strength was 150 kg/mm² after tempering at 300°C for 1 hr.

With the exception of the case in air, water, or HCl solution of pH 5, there can be seen the existence of a critical stress under which the fracture time is considerably prolonged. The critical stress may be realized extending the testing period even in air, water, or HCl solution of pH 5. The resembling results are shown in Fig. 3 for steel *D-1* with tensile strength of 125 kg/mm² after tempering at 550°C for 1 hr. The suppressed fracture time in 0.1 N HCl solution at low applied stresses are probably attributed to the increase of actual stress owing to the reduction of the cross sectional area from the general corrosion.

The fracture strength under a sustained load in air is little decreased comparing with the static bending

strength. The delayed fracture strength of both steels decreased in HCl solution with the increasing acidity, and decreased remarkably in the solution containing H₂S, as the results reported by some investigators.^{5),6)}

The appearances of delayed fracture surface of steel *B* in each environment are shown in Photo. 1. Fracture occurred at the tensile side of the specimen, and there can be seen a shear lip near the surface in all environments. Photograph 2 are images of fracture surface by a scanning electron microscope, and these photographs show that the crack propagates in the shear type fracture near the surface and in the cleavage like fracture at the interior of the specimen. Photograph 3 shows an under-surface crack obtained at the early stage of delayed fracture test. These facts suggest

Fig. 3. The relation between applied stress and time to failure for steel *D-1* in various environments under sustained load Fig. 2. The relation between applied stress and time to failure for steel *B* in various environments under sustained load

Fractured after 89.5 hr in air 22.7 hr in water 49.8 hr in 0.1N-HCl 33.9 hr in 0.1% NaCl 17.3 hr in 3% NaCl

Photo. 1. Fracture surface under sustained load in various environments showing a shear lip at the tensile side of the specimen (arrows) (×5) (×3/4)

Photo. 2. Scanning electron microscopic observations of fracture surfaces broken under sustained load in the air (top) after 90 hr and in water (bottom) after 240 hr

Photo. 3. Under surface crack observed on the axial section of the specimen after sustained loading in 0.1 N HCl solution

that the crack originated under the surface, propagated in the cleavage like fracture, then turned to the shear type fracture arriving to the surface of the specimen.

The behaviour of the initiation and propagation of the delayed fracture in the present investigation resembles that of the delayed fracture induced from hydrogen.⁷⁾ Table 2 shows the results of hydrogen

Table 2. The results of hydrogen analysis of steels dipped in various environments

Environment	Dipping time (hr)	Hydrogen content (ml/100 g)	
		Steel D-1	Steel B
Air	—	0.24	0.22
pH-HCl soln.	50	0.28	0.18
3% NaCl soln.	100	0.66	1.03
0.1 N HCl soln.	50	2.87	2.20
0.5% HAc + H ₂ S	50	7.06	9.36

analysis of steels dipped in various environments. Specimens used were 6 mm in diameter and 70 mm in length. Hydrogen was extracted at 1 000°C. When hydrogen absorption of the steel is the more remarked in such a solution, the delayed fracture strength of the steel decreases the more.

Hughes *et al.*¹⁾ showed from their polarization experiment that the fracture strength of low alloy steels under sustained loads was controlled by hydrogen embrittlement in 0.1 N HCl solution, and by anodic dissolution in NaCl solution. On the other hand, Logan and Wehrung¹⁾ reported that hydrogen permeated through the steel when AISI 4340 steel exposed to boiling NaCl solution.

In the present investigation, the increase of hydrogen content was confirmed also in the specimen dipped in NaCl solution at room temperature. Furthermore, shear lips were found, which showed that fracture initiated at the interior of the specimen, even in NaCl solution. A possible explanation for the difference from the result by Hughes *et al.* using unnotched specimens is that the stress induced diffusion of hydrogen at the site of the maximum triaxiality, as proposed by Troiano,⁸⁾ was promoted by the stress concentration in notched specimens, and a dangerous level of hydrogen concentration reached more easily than plane specimens.

It can be expected that the thickness of a shear lip indicates approximately the depth from the surface to the origin of the delayed fracture crack. Specimens of steel B with various notch radii between 0.03 and 0.1 mm were fractured under sustained load in 0.1 N HCl solution. It was confirmed that the thickness of shear lips coincides with the positions of the maximum triaxiality. The maximum triaxiality position was estimated as the maximum point of elastic radial stress after Neuber's solution.⁹⁾

The delayed fracture strength of steel B in water was almost the same as in HCl solution of pH 5, as shown in Fig. 2. The water had been purified to about pH 6.8 at first by a de-ionizer, but the pH value of the water changed to pH 4 to 5 after about 40 min, on exposing to air in the laboratory and in outdoors. This acidification of the water is probably attributed to dissolution of such gases as CO₂ and SO₂ in air, and may explain another reason why the fracture appearance was preferred to hydrogen embrittlement in water and even in NaCl solution in the present investigation.

Fig. 4.

Stress vs. fracture time curves under sustained load in 0.1 N HCl solution for steel D

These facts mentioned above suggest that the test in weak acidic solution is effective to examine the delayed fracture behaviour of steel products with notches in the moist air.

2. Influence of Tempering Temperature

The stress vs. fracture time curves in 0.1 N HCl solution for steel D on tempering at various temperatures are shown in Fig. 4. Specimens tempered at low temperature show a drastic loss in the fracture strength at a short time, while specimens tempered at higher temperature lose a little in the fracture strength for a long period of loading. Curves for specimens tempered at high temperatures fall slowly after several ten hours because of the increase of an actual stress owing to the loss of the sectional area from general corrosion. Accordingly, the stress at which fracture occurs after 30 hr (named 30 hr strength) was selected in the present work as the characteristic value representing the resistance of the steel to delayed fracture, because, under this condition, general corrosion had little effect on the fracture strength and the time to fracture had increased rapidly.

Figure 5 shows the change of delayed fracture characteristics in 0.1 N HCl solution and static bending strength with tempering temperature. The static bending strength varies rather in simple manner with increasing tempering temperature, and 30 hr strength varies complicatedly. But characteristically, there appear two peaks in 30 hr strength on tempering at 200° to 300°C and at the higher temperature, and a depression at about 350°C between both peaks. Allread and Robinson¹⁰⁾ for cathodically charged steel, Davis *et al.*¹¹⁾ for steel in NaCl solution, and Hughes *et al.*¹⁾ for steel in HCl solution, respectively, reported a similar peak or a depression in the delayed fracture strength on tempering at low temperature. Hughes *et al.* explained this peak as epsilon carbides trapped hydrogen in steel.

Though epsilon carbides were not ascertained in the steels used, the possibility of generation of epsilon

Fig. 5. The change of static bending strength, delayed fracture strength in 0.1 N HCl solution and its ratio to static bending strength with tempering temperature.

carbides was shown by Altstetter¹²⁾ for low carbon steels such as steel A or B.

The peak at the lower tempering temperature for steel B containing a large quantity of silicon, is shifted at higher tempering temperature than the peak for steel A containing a small quantity of silicon. This phenomenon may be explained as the effect of silicon¹³⁾ to retard the decomposition of epsilon carbides.

Beyond the peak in 30 hr strength at the higher tempering temperature, the ratio of 30 hr strength to static bending strength (named strength ratio in delayed fracture) stays at a constant and high value for all steels. This result implies that the decrease in 30 hr strength with increasing tempering temperature beyond the peak at the higher tempering temperature was not attributed to the increase in the sensitivity to delayed fracture of the steel, but to the decrease in load carrying capacity (*i.e.* the static bending strength).

Figure 6 shows the relation between the hardness and the strength ratio in delayed fracture. There appears that the strength ratio depends mainly on the hardness of the steel. Peaks at 350 and 450 in Vickers hardness for steels *A* and *B*, respectively, are the same as peaks at the lower tempering temperature mentioned earlier.

Fig. 6. The relation between hardness and strength ratio of delayed fracture in 0.1 N HCl solution

3. Characteristics in Hydrogen Embrittlement

The variation of the sensitivity to hydrogen embrittlement with tempering was examined for steels *B* and *D*, because of the consideration that hydrogen embrittlement has an important role in the delayed fracture of the steel in HCl solution.

Tensile tests were carried out for test pieces dipped in 0.1 N HCl solution for 5 hr followed by aging for 2 hr at room temperature. The results are shown in Fig. 7 for steel *B*. The tensile strength and the proof stress are not varied by dipping the test piece in 0.1 N HCl solution, but the elongation and the reduction of area are decreased considerably. Polishing the test piece to eliminate the surface pits by chemical attack has no effects to decrease the embrittlement. The ductility of the test piece is recovered by heating at 150°C for 17 hr.

The degree of embrittlement was estimated from the reduction of area of test pieces with and without dipping. The results are also shown in Fig. 7. The behaviour of the variation in the degree of embrittlement with tempering is in good similarity to that in the delayed fracture strength. The same relation was also obtained for steel *D*.

4. Observation of Crack Path

Crack propagation path in delayed fracture in 0.1 N

Fig. 7. The change of tensile properties with tempering temperature for steel *B* dipped in 0.1 N HCl solution for 5 hr followed by aging for 2 hr at room temperature

HCl solution for steel *B* are shown in Photo. 4. Specimens were austenitized at 1200°C for 30 min to coarsen the austenitic grain size for convenience in observation of the crack path. Delayed fracture tests were interrupted after an appropriate period of test, and cracks were observed on the axial section of the specimen.

There can be seen that the crack propagates along the austenitic grain boundaries in the specimen tempered at 400°C where the delayed fracture strength was depressed abnormally, and the crack propagates transversely in prior austenitic grains for other specimens tempered at 250° and 500°C. The same features of crack propagation path were confirmed also for steels *A* and *D*. And many of minor cracks along austenitic grain boundaries were observed for steel *D* even if tempered at 500°C. These facts indicate that the strength of the prior austenitic grain boundaries plays an important role in delayed fracture from hydrogen embrittlement.

An extraction replica image for steel *B* tempered at 400°C is shown in Photo. 5. It appears that the continuous carbides precipitated along the prior austenitic grain boundaries are a peculiar condition corresponding to the depression of the delayed fracture strength. A similar condition of carbide precipitation is observed also in Photo. 6 for steel *D* tempered at 450°C.

IV. Summary and Conclusion

The results of the investigation of the delayed fracture characteristics in several corrosive environments

Photo. 4.

Crack propagation path in delayed fracture in 0.1 N HCl solution for steel *B*, showing transcrystalline fracture ((a) and (c)) and intercrystalline fracture (b). Etched by saturated picric acid solution ((a) and (c)) or 1% nital (b). ($\times 100$) ($\times 4/5$).

- (a) 250°C tempered
- (b) 400°C tempered
- (c) 500°C tempered

Photo. 5.

Electron micrographs of extraction replica for steel *B* with tempering at 400°C, showing carbide precipitation at prior austenite grain boundary (A) and flaky cementites (B).

Photo. 6.

Electron micrograph for steel *D* with tempering at 450°C, showing grain boundary precipitation of carbides (arrows).

for low alloy steels hardened and tempered, are summarized as follows:

The low carbon martensitic steel and the medium carbon sorbitic steel with tensile strength of 150 kg/mm² and 125 kg/mm², respectively, do not fail in the atmosphere under sustained load if the applied stress is not high enough as just below the static bending strength. The delayed fracture strength of the steel, however, decreases in contact with water, NaCl solution, HCl solution, and acetic acid solution containing H₂S. Hydrogen contents of the steel increases on dipping in these environments. On the other hand it was observed that the delayed fracture crack originated under the surface at the notch root.

These facts suggest that the delayed fracture in these environments is attributed mainly to hydrogen embrittlement induced from the electrochemical reaction between the steel and the environments, with the exception of the case that the testing period is extremely prolonged and the decrease of the cross sectional area from corrosion plays an important role.

The dependence of the delayed fracture characteristics in 0.1 N HCl solution for several low alloy steels on the tempering temperature was investigated. The results are summarized as follows:

The delayed fracture strength decreases depending mainly on the increase in the hardness above V.H.N. 350. But the peak of the delayed fracture strength is obtained for the steel tempered at 200° to 300°C, and an abnormal depression for the steel tempered at about 350°C. For the steel containing much amount of silicon, the peak of the delayed fracture strength shifts to the higher tempering temperature. A similar feature was obtained in the variation of the degree of hydrogen embrittlement with tempering of the steel dipped in 0.1 N HCl solution.

These facts suggest that the delayed fracture strength in 0.1 N HCl solution depends on the change in the metal structure which affects the hydrogen embrittlement of the steel, and that the change of delayed

fracture strength and selective crack propagation path are related to the precipitation behaviour of the carbides at the prior austenitic grain boundaries.

It is not clear that the change of metal structure on tempering was attributed to the delayed fracture strength whether directly through the sensitivity to the hydrogen embrittlement or through the change of chemical and electrochemical properties of the steel. These are important problems to be resolved in the future study.

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