

**Mechanistic aspects of hydrogen induced cracking
in structural steels under hostile environments**

2004

JOO HAENGSIK

Contents

Nomenclature.....	i
--------------------------	----------

Chapter 1 General Introduction

1-1 Delayed fracture mechanisms in high and low strength steels.....	1
1-2 Outline of the present dissertation.....	6

Chapter 2 Mechanistic aspects of delayed fracture of the thin specimens of steels

2-1 Introduction.....	10
2-2 Experimental procedure.....	12
2-3 Results and Discussion.....	14
2-3-1 Influence of the reduction in specimen thickness on delayed fracture time.....	14
2-3-2 Influence of the reduction in the specimen thickness on crack initiation and propagation.....	15
2-3-3 Influence of specimen thickness on the depth of crack origin and on the numbers of QC facets in the fracture surface.....	16
2-3-4 Stable crack growth in thin plate and thin walled hollow specimens and classical Griffith type equation.....	18
2-3-5 Influence of specimen thickness on delayed fracture time.....	20
2-4 Summary.....	21

Chapter 3 Mechanistic aspects of hydrogen degradation in high and low strength steels

3-1 Introduction.....	50
3-2 Experimental procedure	51
3-3 Results and Discussion.....	54
3-3-1 The susceptibility to delayed fracture in steels.....	54
3-3-1-1 Relationship between the susceptibility to delayed fracture and the yield strength in steels.....	54
3-3-1-2 Relationship between the susceptibility to delayed fracture and the change in the morphology of crack propagation.....	55
3-3-2 Influence of the mechanistic factor on the development of IG crack.....	57
3-3-2-1 Relationship between the crack tip configuration and IG crack	

development.....	57
3-3-2-2 Relationship between the crack tip blunting and IG crack development in high strength steels.....	58
3-3-2-3 Relationship between the tempering temperature and IG crack development.....	60
3-3-3 Mechanisms of QC crack development to delayed fracture in steels....	61
3-4 Summary.....	62

Chapter 4 Crack initiation mechanisms at welded joints under hydrogen attack

4-1 Introduction.....	82
4-2 Experimental procedure.....	84
4-3 Results and Discussion.....	85
4-3-1 Feature of microstructures at the welded joints.....	85
4-3-2 Delayed fracture characteristics of welded joints	85
4-3-3 Difference in susceptibility to delayed fracture between the base metal and the weld metal	87
4-3-4 Difference in crack propagation mechanisms between the base metal and the weld metal.....	89
4-3-5 Role of blowholes in weld metal under hydrogen attack.....	91
4-4 Summary.....	93

Chapter 5 Conclusions and Further work

5-1 Conclusions.....	114
5-2 Further work.....	117

Acknowledgements.....	119
------------------------------	------------

List of References.....	120
--------------------------------	------------

List of Publications and Presentations.....	127
--	------------

NOMENCLATURE

The symbols most commonly used in text are listed below

d	Diameter of round bar solid specimen
D	Hydrogen diffusion coefficient in Fe
H	Thin walled hollow specimen
L_{QC}	QC crack facet length
r_p, r_s, r_h	Depth of crack origin from the specimen surface in the thin plate, round bar solid and thin walled hollow specimens
S_{area}	Cracked area of QC facet
t_p, t_h	Thickness of thin plate and thin walled hollow specimens
σ_f	Nominal fracture stress
σ_{th}	Threshold stress under delayed fracture
σ_{UTS}	Ultimate tensile strength
σ_y	Yield strength

The abbreviation most commonly used in text are listed below

A-A'	Section of the thin plate specimen
AF	Acicular ferrite
BM	Base metal
GF	Grain boundary ferrite
HAZ	Heat affect zone
HE	Hydrogen embrittlement
HIC	Hydrogen induced cracking
IG	Intergranular
MAG	Metal active gas
MVC	Micro-void coalescence
NCOD	Normalized value of crack origin depth
NPC	Non-propagating crack
QC	Quais-cleavage
Q/T	Quenched and tempered
R.B	Round bar solid specimen
R.A	Reduction in area
SEM	Scanning electron microscope
SL	Shear lip
SSCC	Stress sulfide corrosion cracking
TG	Transgranular
WF	Widmanstaetten ferrite
WM	Weld metal
α	Ferrite
$\alpha+\theta$	Pearlite

Chapter 1

General Introduction

1.1 Delayed fracture mechanisms in high and low strength steels

Delayed fracture in steels and alloys

It is well recognized that the susceptibility to delayed fracture of structural steels becomes greater with the increased ultimate tensile strength (σ_{UTS}) and that a remarkable decrease in the delayed fracture strength of steels is quite noticeable in the strength level beyond a particular σ_{UTS} ranging from 1300MPa to 1600MPa, as shown in Fig. 1-1[1]. Such high strength steels are often used as structural components or device materials in aggressive environments. Structural materials are generally required to have a high yield strength level, and various fracture preventive measures have been proposed to prevent embrittlement fracture, which causes a catastrophically rapid fracture in materials at up to the speed of sound. In many materials, the susceptibility to hydrogen embrittlement grows with increasing a strength level [2]. In this sense, an analysis of the fracture process under aggressive environments is essential to understand the nature of fracture and to have an appropriate knowledge for fracture prevention. In general, the delayed fracture mechanism is very important in understanding and characterizing the hydrogen susceptibility of high strength steel products, such as screw bolts, etc. [3].

A study on delayed fracture in steels and alloys

Delayed fracture mechanisms are complicated phenomena, compared to other

types of fractures, or cracking under environmental influence that may alter stress state built up ahead of crack tip. Any attempts to evaluate correlations between cracking behavior and material properties should take interaction effects between environmental and mechanistic parameters into consideration. Most of the delayed fracture mechanisms lying in the crack propagation process of steels and alloys involve a strong interaction between hydrogen accumulation and stress state built up in a local stress concentration region. The hydrogen behavior in a local plastic flow may be complicated, depending on the structure and properties of the material such as microstructures obtained by various heat treatments, mechanistic conditions such as plane stress/strain conditions, whether the specimen is notched or unnotched, as well as environmental factors such as temperature, and diffusion and concentration of hydrogen. Therefore, researchers' attention is primarily focused on the influence of each factor on the mechanisms of interaction between hydrogen and the development of initial crack. There are many reports on crack propagation, dislocation, and plastic deformation with emphasis on mechanistic factors [4-5], diffusion of hydrogen in steel with emphasis on environmental factors [7-10], microstructure [11] and carbide formation [12], and influence of the P and S elements [13-14] with emphasis on material factors. Furthermore, the introduction of solute hydrogen in high purity aluminum was studied using electrochemical charging and chemical charging [15]. Hydrogen trapping in high-strength steels was researched using a potentiostatic pulse technique [16]. The ultra fine grained steel with an average ferrite grain size of 0.3 μm and oxide particles of 10 nm showed high resistance to hydrogen embrittlement by hydrogen trapping effect related to the nanosize oxide particles [17]. The finite element method [18-29] is a useful tool for modeling the effect of hydrostatic stress and hydrogen trapping due to

plasticity on the hydrogen distribution ahead of crack tip. On the other hand, there still remains the critical issue of a comprehensive understanding of the delayed fracture due to hydrogen in steels, despite many approaches of investigations [30].

Hydrogen diffusion in solids

The hydrogen behavior in solids has long been a major concern in research on delayed fracture mechanisms. Völkl and Alefeld have summarized the behavior of the hydrogen diffusion in Fe [31]. Yet, there is no clear agreement concerning the influence of hydrogen diffusion on the mechanical properties of engineering alloys. Therefore, most of the academic attention is focused on the influence of hydrogen on the mechanical properties of iron and steel. Some earlier works gave us two completely different concepts of the role of hydrogen: one is softening iron [32-34], the other is hardening iron [35-41]. On the other hand, in order to discuss the interaction between hydrogen influence and delayed fracture mechanisms in crack propagation of steels, it is necessary to consider its diffusivity and solubility in steels. On the basis of the Völkl and Alefeld criterion, Hirth suggested the hydrogen diffusion coefficient (D) in Fe [42].

A study on fracture mechanisms under hydrogen attack

There are several basic theories of hydrogen behavior in embrittlement mechanisms: the pressure theory [43], the decohesion theory [44], and the hydrogen enhanced local plasticity theory [45]. Hydrogen embrittlement generally requires local concentration of hydrogen at voids or crack tips, where hydrogen accumulates at trap sites such as defects, interfaces between different phases, grain boundaries, and at dislocations [46-51]. Certain local concentration of hydrogen brings about the nucleation of voids that is assumed to be made by the effect of hydrostatic stress with

the physicochemical properties of the structure. The hydrogen transport model of Sofronis and McMeeking [52] proposed the hydrostatic stress state and trapping effects of hydrogen near the crack tip. In this model, it is assumed that hydrogen atoms diffuse through lattice sites, and that trap sites are filled in through the lattice diffusion. These trap sites are mostly formed due to small local plastic deformation. Krom et al [53] made a new proposal for the definition on the hydrogen distribution ahead of a crack tip based on the earlier model of Sofronis and McMeeking, using the finite element analysis incorporating the effect of hydrostatic stress and the trapping of hydrogen coupled with diffusion elastic-plastic stress.

On the other hand, an examination of the crack propagation capability with respect to the crack tip shape or plastic deformation caused by hydrogen behavior is also important in understanding the contribution of hydrogen at the crack tip in relation to the crack initiation and growth mechanisms. Since the crack development is associated with stress induced hydrogen diffusion near stress raiser such as notches and defects, many experimental studies have been made on various dimensions of particular specimens which have an artificial stress raiser such as a notched and pre-cracked specimen that simulates the screw bottom of a bolt, with emphasis on the macroscopic crack propagation behavior and the fracture mechanics technique [54-55].

Stress intensity factor and hydrogen accumulation

There have been many endeavors on correlative analysis of hydrogen cracking and crack propagation phenomenon, using notched specimens which are widely, accepted for the study of high strength ductile materials [56-59]. The stress intensity factor (K) to describe the stress condition at the crack tip is very useful in explaining the correlation between the stress concentration and the hydrogen accumulation behavior around the

crack tip [60-61]. Many attempts have been made to evaluate the threshold values of K for hydrogen cracking, and to establish a relationship between the threshold K values and hydrogen effects of hydrogen concentration behavior on crack tip [62-66]. However, the importance of the correlation between the crack tip concentration of hydrogen and the crack growth path in the microstructure is not well explained due to insufficient understanding of the hydrogen condensation behavior around the crack tip.

Fractographic analysis

It is particularly difficult to observe the crack initiation behavior in the subsurface of a specimen and crack propagation due to a hydrogen accumulation around the defects such as non-metallic inclusion, lath or packet boundary of the prior austenite grains [67], carbide etc. No appropriate technique is available to study the crack propagation mechanisms except through fractographic analyses on the fracture surface [68].

The morphologies of the crack propagation in fracture surface of high strength steels under hydrogen environment are known as delayed fracture, which can be characterized by the Inter-Granular (IG) crack facet [69-70]. Many studies of crack propagation behavior, particularly using the notched or pre-cracked specimen shape, have provided valuable evidence for macroscopic crack initiation and development, which are useful in understanding crack propagation mechanisms caused by the combined effects of hydrogen accumulation and stress concentration in the front of the artificial crack tip.

HIC and SSCC fracture mechanisms in low strength steels

When hydrogen permeates through the surface of steel and precipitates in the interfaces between matrix and non-metallic inclusions or between matrix and defects, these irregularities can be a nucleation point of cracking [71]. Hydrogen induced

cracking (HIC) may also occur in low to medium strength steels and alloys, conventionally used for pressure vessels and piping in the oil, natural gas and chemical industries [72]. This form of hydrogen damage has also been called hydrogen induced blistering cracking. HIC and stress sulfide corrosion cracking (SSCC) due to hydrogen accumulation around the local deformation has been a great concern [73-81] in service.

IG and TG crack in high and low strength steels

Previous studies [39] have investigated the crack propagation in the delayed fracture of high and low strength steels. These results using notched specimens of high strength steel revealed that the IG crack first initiated at the front of a very sharp crack tip triggers fracture. On the other hand, the Trans-Granular (TG) crack first nucleated at the subsurface, as an initial crack mode in low strength steel. It seems clear from these studies so far that the delayed fracture mechanisms may be different in high and low strength steels [82-83] from the viewpoint of crack propagation behavior.

1.2 Outline of the present Dissertation

Although many studies have been performed for the analysis of delayed fracture mechanisms using notched specimens or specimens with artificial stress raisers, as shown in Fig. 1-2, and also have focused on the hydrogen diffusion and concentration ahead of the artificial crack tip, some essential problems remain unsolved regarding the particular mechanisms of initial crack development. This dissertation employs unnotched specimens instead of notched specimens to make careful understanding of the initial crack development and its mechanisms, using the SEM fractographic methods.

The present dissertation consists of five chapters including this introductory chapter. In chapter 2, the influence of localized stress conditions on hydrogen induced cracking was studied by employing extremely thin specimen in high strength steels.

In chapter 3, crack propagation mechanisms of high and low strength steels under sustained load with hydrogen were investigated with emphasis on the influence of the various levels of yield strength, which were obtained by changing the heat treatment temperature.

In chapter 4, hydrogen embrittlement behaviors of the weld metal and the base metal were studied with an emphasis on the susceptibility to delayed fracture and initial crack development, and propagation mechanisms in fracture using the various types of unnotched specimens.

In chapter 5, conclusions and further work are mentioned briefly.

Chapter 2

Mechanistic aspects of delayed fracture of the thin specimens of steels

Abstract

To examine an influence of the localized mechanical effects introduced by the difference of specimen configurations on the fracture lifetime and the initial crack development behavior of the ASTM A490 and S35C steels, delayed fracture tests were carried out under hydrogen attack using thin plate specimen, smooth solid bar and thin walled hollow specimens. Cathodic hydrogen charging was used for introducing hydrogen in the specimen under sustained load conditions. The lifetime under delayed fracture depends on the specimen thickness. A brittle fracture due to hydrogen attack still occurs in extremely thin thickness, $t=0.3\text{mm}$, of the thin plate and thin walled hollow specimens. The QC cracks in the thin plate and thin walled hollow specimens, still develops at the subsurface of the specimens and the origin of cracks moves from the near surface to the center of specimen as the specimen thickness becomes thinner. The condition for brittle fracture in delayed fracture can be evaluated by the classical Griffith criterion employing fracture stresses and QC crack lengths. The amount of hydrogen damage caused by the difference in localized mechanistic conditions makes the difference in fracture lifetimes between thick and thin specimens.

Key Words: Hydrogen Embrittlement, Plane stress, Plane Strain, Quasi-Cleavage Crack, Intergranular Crack

2-1 Introduction

Hydrogen penetrates into high strength steel components or structural materials used for bridges or factory plants such as a large steel-bridge built across a wide river or channel and chemical or oil plants. Hydrogen accumulates at the stress concentration zone in structural components and plays an important role in making an initial crack

causing unexpected embrittlement fractures. Investigations of the brittle fracture mechanisms due to hydrogen attack have been actively carried out with a focus on the phenomenological approach using a notched specimen to simulate a particular condition in practical use [84]. Evaluation of the crack propagation mechanisms which are studied on the basis of fractographic analysis has been carried out with a focus on the mechanisms of IG crack development at the stress raiser such as precrack or notch and on the role of IG crack in the crack propagation period [85-91].

On the other hand, earlier works on the delayed fracture under sustained load tests, particularly using the smooth specimen of ASTM A490 steel, SNCM 439 steel and S35C steel without any artificial macroscopic stress raisers [92-95], have revealed that the brittle fracture definitely occurs at the low applied stress less than their yield strength levels, i.e., less than 1/10 of the yield strength level in the case of SNCM 439 steel as shown in Fig. 2-1 [96] and Fig. 2-2 respectively.

According to these studies [96-100] quasi-cleavage (QC) cracking was found to be as essential as IG crack which has been so far accepted as the essential crack in hydrogen related fracture [101] as shown in Fig. 2-3. SEM fractographic examination revealed that the size of QC crack facet could be regarded as the critical length of the Griffith crack in the delayed fracture. Furthermore, the mechanistic aspect of brittle fracture condition for delayed fracture can be simply evaluated by the classical Griffith criterion employing both the critical crack length (L_{QC} : m) and the nominal fracture stress (σ_f : MPa). The length of the QC crack facet satisfies the classical Griffith type equation given by [102]:

$$\sigma_f \cdot L_{QC}^{0.51} = 6.2 \dots\dots\dots(2-1)$$

(σ_f : Nominal fracture stress [MPa], L_{QC} : QC crack facet length [m])

However, the initiation and development processes of the QC crack still remain unclear, although it plays an important role on the critical crack growth behavior as the trigger to the onset of the unstable crack growth involving IG crack or micro-void coalescence (MVC) leading to the final fracture of specimen. Among the variety of crack growth behavior, characteristic of the QC crack growth behavior can be critical to understand the reason for the total fracture life of specimens.

A critical behavior of the crack growth under hydrogen attack is determined by the hydrogen diffusion and concentration near defects inside the specimen. A question arises as to the difference of the mode of crack development in thick and thin specimens where the macroscopic stress condition is nominally the same. In order to examine an influence of the localized stress condition introduced by the difference of the specimen dimension on the development of the initial crack in the delayed fracture of the Q/T ASTM A490 and S35C steels, sustained load fracture tests were carried out under hydrogen attack using solid bar, thin plate, and thin walled hollow specimens without any artificial stress raiser.

2-2 Experimental procedure

The materials employed in this study were the high strength steel of ASTM A490 and S35C steels with chemical compositions as shown in Table 2-1. ASTM A490 steel was machined into thin plate shape specimens with a width of 14.5mm and

thickness of 2mm and 1mm respectively as shown in Fig. 2-4-(a). Furthermore, thin plate specimen with thickness of 0.5mm and 0.3mm can be easily influenced by warping, so that we performed heat treatment using the plate specimen of 1mm thickness and then machined it into thin plate specimens of 0.5mm and 0.3mm thickness to avoid the deformation.

On the other hand, S35C steel was machined into hourglass shape specimens with mid-section diameters of 8mm and 5mm respectively, and then was machined into thin walled hollow specimens with outer diameter of 8mm and inner diameters of 7.4mm and 4mm as shown in Fig. 2-4-(b) respectively. To obtain martensitic structure with an average prior austenite grain diameter between $10\mu\text{m}$ to $20\mu\text{m}$, the ASTM A490 steel specimen was first austenitized at 1473K for 2 minutes in an electro-furnace and quenched into salt bath at 1143K for 10 minutes, followed by oil quenching as shown in Fig. 2-5-(a). The S35C steel was austenitized at 1173K for 10 minutes and for 60 minutes in electro-furnace respectively, followed by oil quenching to arrange a quenched martensitic structure as shown in Fig. 2-5-(b). These specimens were then mechanically polished, and then tempered at 473K for 1 hour in vacuum furnace (1.3×10^{-4} Pa) before mechanical testing.

Mechanical properties of the ASTM A490 steel specimen are given in the following: the ultimate tensile strength = 1510 MPa, 0.2% proof stress = 1310 MPa, reduction in area = 55%, and micro-Vickers hardness = 554 Hv (50 points average with 300g indenter). Mechanical properties of the S35C steel specimen are given in the following: the ultimate tensile strength = 1630MPa, 0.2% proof strength= 1330 MPa, reduction in area =50%, and micro-Vickers hardness = 479 Hv (50 points average with 300g indenter).

Specimens were subsequently put into cathodic hydrogen charging through the surface gauge area using a platinum anode in 0.3mol and 0.03mol H_2SO_4 solution for ASTM A490 steel and S35C steel with a current density of 500 A/m^2 at ambient temperature. The specimen surface was covered with shielding tape except the gauge area to prevent attack by H_2SO_4 . It was noted that the crevice corrosion occurs between the specimen surface and shielding tape covering that protected the immersion of sulphuric acid in 0.3mol H_2SO_4 when the specimen becomes thinner than 0.5mm. Then, in the case of S35C steel, hydrogen was carefully charged to the thinner specimen using sulfuric acid of 0.03mol. Consequently, there was no crevice corrosion occurrence in 0.03mol H_2SO_4 , even in the case of the 0.3mm thickness of thin walled hollow specimen of S35C steel.

The delayed fracture experiment of ASTM A490 and S35C specimen was carried out in 0.3mol and 0.03mol H_2SO_4 solution respectively, and all the lifetime data to fracture were compared under the same current density of 500 A/m^2 and each solution concentration. Conventional delayed fracture tests were performed using a 3-ton creep-testing machine under the condition that the mechanical loading began with simultaneous hydrogen charging, and both the current density and H_2SO_4 concentration were kept constant during the test as shown in Fig. 2-6. The trace of crack propagation in the fracture surface of the specimen was examined using scanning electron microscope (SEM).

2-3 Results and Discussion

2-3-1 Influence of the reduction in specimen thickness on delayed fracture time

Figure 2-7 shows the results of delayed fracture tests, giving the relationship between the nominal fracture stress and the time to fracture under hydrogen attack using the plate specimen with four kinds of thickness-- 2mm, 1mm, 0.5mm and 0.3mm of ASTM A490 steel respectively. Figure 2-8 shows the results of delayed fracture tests, giving the relationship between the nominal fracture stress and the time to fracture under hydrogen attack using the unnotched specimens with diameter of 8mm and 5mm and the thin walled hollow specimens of S35C steel with walled thickness of 2mm and 0.3mm respectively. No appreciable differences were observed in the mechanical properties of brittle fracture such as reduction in area (R.A) showing 2% or less of difference in a thin walled hollow specimen and thin plate specimen although the plate and a wall thickness become extremely thin up to 0.3mm respectively. The time to fracture shows a tendency of increase with decreasing plate and wall thickness in both thin plate and thin walled hollow specimens. It is shown in Figs 2-7 and 2-8 that the increase in fracture time comes to be remarkable with the decrease in specimen thickness especially in the case of 0.3mm thickness. It is suggested that this increase in the fracture time must be dependent on hydrogen diffusion and accumulation behavior in front of the initial crack tip caused a change in the specimen size. In order to examine the influence of specimen dimension on the crack propagation behavior, the detail of the cracking process was analyzed with the aid of fractography.

2-3-2 Influence of the reduction in the specimen thickness on crack initiation and propagation

A schematic illustration of the feature of subsurface crack propagation together with the SEM micrograph is shown in Fig. 2-9 which shows no clear identification of

characteristic fracture facets such as the QC and IG cracks typically observed in the fracture surface of solid specimen. Figure 2-10 shows the equivalent feature of crack propagation in thin plate specimen. From these results it is suggested that the initial crack is the QC crack with a circular or elliptical feature rather than the IG crack irrespective of geometry and dimensions of the unnotched specimens. Figs 2-11 and 2-12 show that crack propagation morphologies of schematic illustration of thin plate specimen with thickness of 0.5mm or less and of thin walled hollow specimen with thickness of 0.3mm, and the SEM fractograph of the QC initial crack facets respectively. The crack propagation in thin plate specimen with thickness of 0.5mm or less and in thin walled hollow specimen with thickness of 0.3mm gives a result different from that of the thick plate and thick walled hollow specimens with thickness of 1mm or more.

In the case of specimens having thickness larger than 1mm, a single QC crack usually grows as a trigger and unstable crack growth involving IG crack and MVC follows as shown in Fig. 2-9 and Fig. 2-10. In the case of thin plate specimens with thickness of 0.5mm or less and of thin walled hollow specimen with thickness of 0.3mm, multiple QC cracks coalesce each other until they reach the critical length followed by the fatal growth involving the IG crack and MVC leading to final fracture as shown in Fig. 2-11 and Fig. 2-12 respectively. The QC facets also show an irregular crack growth on the surface along the direction of width in thin plate specimen and along the direction of circumference in thin walled hollow specimen as shown in Fig. 2-11 and Fig. 2-12 respectively. This may be due to the localized crack tip constraint in the direction of thickness of the specimen [103].

2-3-3 Influence of specimen thickness on the depth of crack origin

and on the numbers of QC facets in fracture surface

It is interesting to know that the initial crack still originated in a similar manner as the thick or solid bar specimens, at the subsurface of specimens that were carefully machined to have an extremely thin thickness of 0.3mm in both thin plate and thin walled hollow cylindrical specimens. The crack origin moved from the near surface to the center of specimen as the wall thickness become thinner where the plane stress condition clearly dominates regardless of the specimen geometry for ASTM A490 and S35C steels. To explain the relationship between the wall thickness of specimen and the depth of crack origin from specimen surface, the fracture surface of both specimens were carefully examined. The relationship between the normalized depth of the crack origin and the wall thickness of specimens are shown in Fig. 2-13 and Fig. 2-14 respectively. The normalized value of the depth of crack origin is defined by dividing the depth of crack origin by the half of the specimen diameter “d” for the solid specimen, and by the half of the wall thickness of the specimen “ t_p ” and “ t_h ” for the plate specimen and the thin walled hollow specimen as shown in Fig. 2-15 and Fig. 2-16 respectively. The normalized value obtained tends to vary from 0 to 1 as thickness reduce regardless of specimen geometry for ASTM A490 and S35C steels as shown in Fig. 2-13 and Fig. 2-14 respectively. The value 1 means that the crack origin is at the center of specimen thickness, while the value 0 means that the crack origin is at the surface of specimen. These figures also show an interesting result that the point of crack origin in extremely thin specimens with thickness of 0.3mm is not in the outer surface but still in the subsurface of the specimen. This suggests that the hydrogen crack initiation in structural steels would be deeply related to the hydrogen pressure that possibly build up with the condensation of hydrogen [104] at the defect located at the subsurface of specimen. In

addition, particular attention should be given to the number of cracks that present valuable information on how the crack initiates and propagates in thin specimens under hydrogen attack.

To evaluate the relationship between the numbers of QC cracks and the specimen thickness, the fracture surfaces of specimens having various dimensions of thickness were carefully examined through SEM micrographs. The results of the relationship between the numbers of QC cracks and the thickness of specimens are shown in Fig. 2-17 and Fig. 2-18 with various types of specimens such as plate, solid bar, and thin walled hollow cylindrical specimens. These figures show that the observed number of QC facets on the fracture surface, increases with the decrease for the specimen thickness regardless of the geometry of specimens in ASTM A490 and S35C steels. These results suggest that the critical behavior of hydrogen associated with the crack initiation and propagation would be related to some phenomena with respect to the difference in specimen thickness. Therefore, the maximum length of QC crack as the trigger of unstable crack growth leading to final fracture was investigated to explain the influence of thickness on the critical crack growth and fracture of specimens.

2-3-4 Stable crack growth in thin plate and thin walled hollow specimens and classical Griffith type equation

Although the thickness of plate specimen and the wall thickness of hollow specimen become extremely thin up to 0.3mm, a brittle fracture still occurs and the R.A remains within 2% or less. It is also found that the classical Griffith type equation is still valid with respect to the nominal fracture stress and the maximum length of QC cracks (L_{QC}) obtained from the fracture surface of the thin plate and thin walled hollow

specimens. Since the typical QC crack has an irregular morphology as the plate thickness becomes 0.5mm or less in thin plate specimen and the wall thickness also becomes 0.3mm in thin walled hollow specimen as shown in Fig. 2-11 and Fig. 2-12 respectively. Since the typical QC crack facet as shown in Fig. 2-11 has an irregular morphology in the thin walled hollow specimen of 0.3mm compared with solid specimen, a modified value of the crack length L_{QC} was used as shown in Fig. 2-20-(b), instead of the simple depth of QC facet in the solid specimen and thin plate specimen as shown in Fig. 2-19, 2-20-(a) respectively. A modified L_{QC} was defined as the diameter of a notional circle of the cracked area [105-106] as shown in Fig. 2-20-(b). The relationship between the maximum length of the modified L_{QC} (m) and the nominal fracture stress (σ_f : MPa) of ASTM A490 steel and S35C steel is shown in Figs 2-21 and 2-22 respectively.

The length of the QC crack facet of the ASTM A490 steel satisfies the classical Griffith type equation given by:

$$\sigma_f \cdot L_{QC}^{0.47} = 7.9 \dots\dots\dots(2-2)$$

(σ_f : Nominal fracture stress [MPa], L_{QC} : QC crack facet length [m])

The length of the QC crack facet of the S35C steel also satisfies the classical Griffith type equation given by:

$$\sigma_f \cdot L_{QC}^{0.53} = 7.9 \dots\dots\dots(2-3)$$

(σ_f : Nominal fracture stress [MPa], L_{QC} : QC crack facet length [m])

These results explain that the classical Griffith equation is still valid in the case of extremely thin walled hollow specimen of S35C steel and the thin plate specimen of

ASTM A490 steel.

2-3-5 Influence of specimen thickness on delayed fracture time

Based on mechanical viewpoint, hollow specimens are undoubtedly in a plane stress condition in which the hydrogen behavior may not be under the influence of a particular stress condition. A question arises as to whether the wall thickness of the specimen actually has an influence on the development of hydrogen crack in the thin walled hollow specimens. If the diffusion and concentration behavior of hydrogen are under the influence of the wall thickness of specimen as mentioned in the previous chapter, it can be expected that the fatal QC crack develops at the thick portion, not the thin portion, of the specimen when it has an uneven thickness through the cross section. An eccentrically bored thin walled hollow specimen was accidentally made in which the maximum and the minimum wall thickness were 0.63mm and 0.45mm respectively. The specimen was hydrogen charged for 1080 minutes under the applied stress of 200MPa to develop the QC crack growth in the subsurface of specimen followed by the removal of hydrogen from the specimen by means of heat treatment at 473K for 1 hour in vacuum. The specimen was subsequently subjected to a slow conventional tensile fracture test at a strain rate of about $1 \times 10^{-4} \text{ s}^{-1}$ to avoid unexpected effects due to high strain rate loading, in order to examine the internal crack development caused by the difference in thickness. Figure 2-23 shows a SEM fractograph of QC crack facets and MVC, which were observed in both thick and thin portions of the specimen, and schematic illustration of QC cracks in the fracture surface of the eccentrically bored thin walled hollow specimen. Two or more QC facets were observed in the thick portion as shown in Fig. 2-23.

In the case of the eccentrically bored thin walled hollow specimen that has uneven thickness, the fact that the QC crack is not developed in the thin portion but in the thick portion of the specimen under the same macroscopic aspect of the applied stress condition means that the initial crack due to both the hydrogen accumulation and the applied stress prefers to develop in the thick portion of the eccentrically drilled thin walled hollow specimen. This result denotes that the thick portion has many opportunities to build up localized plane strain stress condition around the vicinity of the non-metallic inclusion or micro-defect, etc., compared with a thin portion of the specimen where the plane stress condition mainly dominates. Namely, it may be concluded that the difference in wall thickness, i.e., plane stress conditions or plane strain conditions is one of the important mechanistic aspects to influence the difference of delayed fracture time in steels.

2-4 Summary

In this chapter, experimental analyses were carried out using various types of specimens to elucidate the influence of the specimen thickness on the initial crack propagation mechanism associated with the hydrogen behavior and on the delayed fracture time using thin plate specimen, solid specimen and thin walled hollow specimen. Results obtained are summarized in the followings:

(1) The fracture lifetime in delayed fracture under hydrogen attack shows a tendency to increase with decreasing thickness of specimens in quenched and tempered S35C steel. This can be explained by the evidence that the initial QC crack prefers to develop

at the thicker section rather than the thinner section of the specimen, which accidentally has both thick and thin section in a single specimen.

(2) Even though the thickness of plate specimen and wall thickness of cylindrical specimens becomes extremely thin up to 0.3mm, the initial crack still develops in the subsurface of specimen. This phenomenon may support the internal pressure theory, which was proposed for the mechanisms of hydrogen related fracture.

(3) The point of crack origin moves to the center of the thickness from near surface of the specimen with a decrease in thickness. The numbers of QC facets, which were observed on the fracture surface decreased with increasing thickness of plate specimen and wall thickness of cylindrical specimen. These results suggest that the hydrogen diffusion and concentration at the initial crack tip is so remarkable compared with the thin specimens in which the crack initiated in subsurface can easily develop to an unstable growth involving the IG crack in the crack propagation period.

(4) Although the thickness of the specimens becomes extremely thin as 0.3mm in the plate specimen of ASTM A490 steel and the thin walled hollow specimen of S35C steel, the brittle fracture condition in delayed fracture can still be evaluated by the classical theory of Griffith by employing the nominal fracture stress (σ_f : MPa) and the maximum crack length of QC cracks (L_{QC} : m). The length of the QC crack facet of the ASTM A490 and S35C steels satisfies the classical Griffith type equation given by:

$$\sigma_f \cdot L_{QC}^{0.47} = 7.9 \text{ (ASTM A490)}, \quad \sigma_f \cdot L_{QC}^{0.53} = 7.9 \text{ (S35C)}$$

(σ_f : Nominal fracture stress [MPa], L_{QC} : QC crack facet length [m])

(5) Under the ordinary stress condition without any artificial stress raiser such as notch, the thickness of specimen is one of the important parameters making influence on the fracture lifetime under hydrogen attack.

Chapter 3

Mechanistic aspects of hydrogen degradation in high and low strength steels

Abstract

Mechanistic aspects of the susceptibility to the delayed fracture were studied with an emphasis on the critical behavior of Quasi-Cleavage (QC) and Inter-Granular (IG) crack growth, which took place inside the specimen. The materials employed were ASTM A490 and S35C steels which were quenched and tempered to have various levels of yield strength ranging 500~1400MPa. These were put into sustained load delayed fracture test with cathodic hydrogen charging. The delayed fracture strength was evaluated by the threshold stress (σ_{th}) at the elapsed time of 10^4 minutes. This σ_{th} value decreased with the increase in the yield strength level and a remarkable decrease was observed beyond $\sigma_y=1000$ MPa. This may be due to the development of crack tip blunting resulting in the non-propagation of crack in low strength steels. The experimental results further suggest that the blunting of crack tip can also be responsible for the absence of IG crack in the crack growth process in low strength steels.

Key Words: Delayed fracture, Susceptibility, Yield stress, Tempering temperature, Threshold stress, Quasi-Cleavage Crack, Inter-Granular Crack

3-1 Introduction

Although high strength steels in practical use have always been required of a high toughness level as well as a high strength level, there still remains a hurdle in achieving a high performance to delayed fracture due to hydrogen attack. The authors have noted from previous studies that the unexpected fracture phenomenon is not unusual in high strength steels such as AISI 4340 and ASTM A490 steels at extremely low stress levels

less than 1/10 of yield strength [107-108] under hydrogen attack. A study on the delayed fracture mechanisms in high strength steels started from the failure of the F13T high strength bolts, which was first reported in 1964 [109]. This accidental event, called delayed fracture or hydrogen embrittlement (HE), is largely due to a combination of stress concentration and hydrogen accumulation at defects such as non-metallic inclusions in the subsurface of a specimen.

It has long been understood that high strength steels have high susceptibility to hydrogen damage even at far below the yield strength level resulting in a catastrophic rapid fracture, or an unexpected fracture known as delayed fracture [110-115] and that the susceptibility to HE and hydrogen-induced cracking (HIC) generally tends to increase as the yield strength of steel increases [116]. On the other hand, some kinds of failure analysis in pipelines for transporting sour gas and offshore pipelines for sour crude oil have made a lot of progress in the research of fracture mechanisms such as HIC and sulfide stress corrosion cracking (SSCC) in low strength steels [117-123].

Now a considerable amount of knowledge has been achieved on the mechanisms of HIC and SSCC caused by hydrogen attack even in low strength steels [124-135]. A morphology of the crack development at an early stage in the fracture surface of high strength steels under hydrogen attack obtained from SEM analyses, can be typically characterized into a category of the Inter-Granular (IG) crack while, in low strength steels, it can be categorized into the Trans-Granular (TG) crack [136]. The reason for the difference of crack initiation morphology in high and low strength steels can be crucial in understanding the critical issue of preventing fracture of structural steels under aggressive environments.

The aim of this chapter is to examine the relationship between the crack

development behavior and the level of yield strength, which has a critical influence on the susceptibility to the delayed fracture. The initiation and development behavior of subsurface crack in high and low strength steels under sustained load tests involving hydrogen attack were studied with a special emphasis on the influence of the level of yield strength on the hydrogen crack development.

3-2 Experimental procedure

The materials employed in this study were ASTM A490 steel, S35C steel (AISI 1035), and API X65 steel with chemical compositions as shown in Table 3-1 and with mechanical properties as shown in Table 3-2 respectively. These materials were machined into unnotched shape with a gauge length and a mid-section diameter of 10mm and 5mm respectively. Details about shape and dimensions of these specimens are illustrated in Fig.3-1 respectively. To obtain martensitic structure with an average prior austenite grain diameter around 10 μ m to 20 μ m, the ASTM A490 steel specimen was first austenitized at 1473K for 2 minutes in electro-furnace and quenched into salt bath at 1143K for 10 minutes, followed by oil quenching as shown in Fig. 3-2. The S35C steel and the API X65 steel were austenitized at 1173K for 10 minutes and at 1273K for 60 minutes in electro-furnace respectively, followed by oil quenching to arrange a quenched martensitic structure as shown in Fig. 3-3 and Fig. 3-4. These specimens were mechanically polished, and then tempered at 473K, 523K, 573K, 623K, 673K, 773K, 873K and 973K for 1 hour in the vacuum furnace with 1.3×10^{-4} Pa to make arrangement of specimens with various kinds of mechanical properties as shown in Table 3-2. Figure 3-5 shows the relationship between the yield strength and the tempering temperature of ASTM A490 steel.

Numerical values of mechanical properties in Table 3-2 are averaged results of at least two or three samples of test specimens. The values of the threshold stresses were also obtained by the delayed fracture test results of 7-10 specimens. Levels of the threshold stress were determined as the largest applied stress at which the fracture did not occur even after the elapsed loading time of 10^4 minutes for each case. On the other hand, in some cases loading was discontinued at the 3×10^3 minutes in ASTM A490 steel since the fracture life curve leveled off at about 10^3 minutes of loading time.

After heat treatment and mechanical polishing, the fatigue pre-cracked specimen with a pit was prepared with electro-discharge machining to have a pit diameter and depth of $150\mu\text{m}$ and $100\mu\text{m}$ respectively, and then $N=10^4$ - 10^5 loading cycles were applied to each specimen under 400MPa which is equivalent to 115%-120% of the fatigue limit estimated from the S-N curve of the ASTM A490 specimen. This fatigue test was carried out in advance of the delayed fracture test at pulsating frequency of 10Hz by MTS electro-hydraulic testing machine. Some of the fatigue pre-cracked specimens were then tempered at 473K for 1 hour in vacuum furnace. Then these specimens were pulled in two types of tension with a 45% and 90% loading of the yield strength level to have blunted crack tip, applying a single load at the strain rate of $10^{-5}/\text{s}$ by MTS electro-hydraulic testing machine in air.

These Specimens were subsequently hydrogen charged cathodically through the surface using a platinum anode in 0.3mol H_2SO_4 solution at a current density of $500\text{A}/\text{m}^2$ and at ambient temperature. The specimen surface was covered with a shielding tape to prevent damage from an attack by H_2SO_4 except the gauge area. Conventional delayed fracture tests were carried out using a 3-ton creep-testing machine under conditions in which the mechanical loading began with hydrogen charging in

H₂SO₄ solution having 0.3mol concentration, and 500A/m² current density was kept constant during the test as shown in Fig. 3-6. A trace of crack path on the fracture surface was then examined using scanning electron microscope (SEM).

3-3 Results and Discussion

3-3-1 The susceptibility to delayed fracture in steels

3-3-1-1 Relationship between the susceptibility to delayed fracture and the yield strength in steels

Sustained load fracture tests with the above hydrogen charging condition were carried out for all kinds of specimens as shown in Table 3-2. Figure 3-7 shows the relationship between the fracture stress and the time to fracture under hydrogen attack using unnotched ASTM A490 specimens in a typical example of the delayed fracture tests. The results of delayed fracture tests for S35C specimens are also shown in Fig. 3-8. These fracture curves of ASTM A490 steel and S35C steel shown in Fig. 3-7 and Fig. 3-8 approximately level off at the elapsed time of about 10³ minutes so that applied load was discontinued at 10⁴ minutes with the exception of ASTM A490 steel specimen where loading was discontinued at the 3x10³ minutes. Threshold stress (σ_{th}) was then determined as the largest value of the applied stress at the elapsed time of 3x10³ or 10⁴ minutes. All the obtained data of the threshold stress of these specimens were given in table 3-2 and Fig. 3-9 showing that these threshold stress increase with decrease of yield strength level due to tempering treatments. Furthermore, in both cases of ASTM A490 steel and API X65 steel specimens, which have the yield strength ranging between 600MPa and 700MPa, the results of the fracture tests clearly indicated that the brittle fracture definitely occurred under hydrogen attack, even under the condition

that the applied stress levels were far below the yield strength of the specimens.

To have a comprehensive understanding from these results, we made an attempt to normalize the relationship with the threshold stress values (σ_{th}) divided by the yield strength (σ_y). The results show that the normalized delayed fracture strength decreases with the increase in the yield strength level for all kinds of steels, and a remarkable change in susceptibility can be seen at the yield strength ranging above $\sigma_y = 1000\text{MPa}$ as shown in Fig. 3-10. Since these results imply that the dramatic reduction in the delayed fracture strength is closely related to the high yield strength, we tried to examine the degradation mechanisms, which is common to all steels in delayed fracture having a wide range of yield strength levels. Then, to examine the detailed aspects of crack development during the fracture process, which is not observed in the surface but in the subsurface of the specimen, fractographic analysis with SEM was mainly employed on the fracture surface of the specimens.

3-3-1-2 Relationship between the susceptibility to delayed fracture and the change in the morphology of crack propagation

In the case of delayed fracture of high strength steels such as quenched and tempered AISI 4340 specimens [92], a characteristic feature of crack growth behavior gave us a notable information that the crucial crack is QC crack developed as the initial crack in subsurface of the specimen rather than the simple IG crack development. Although the IG crack has long been regarded as a critical crack leading to a premature fracture in high strength steels due to hydrogen attack, a fractographic analysis on the fracture surface showing a typical brittle manner of fracture revealed quite an important presence of the notable QC fracture facet showing that fatal growth began

as shown in Fig. 11-(a).

On the other hand, in the case of low strength steels such as API X65 steel, ASTM A490 steel, and S35C steel, which were tempered at relatively higher temperature above 773K after quenching, the specimens show higher resistance to delayed fracture, namely, low susceptibility to delayed fracture. This low susceptibility to delayed fracture should be related with some factors that dominate the essential nature of crack growth. The characteristic feature of crack growth under hydrogen attack has long been considered to be dependent on the yield strength level of steels, such that no IG crack is appreciable in the fracture surface of low strength steels and that IG crack is noticeable in high strength steels [84]. However, a careful examination of crack development and growth morphologies shown in Fig. 3-11-(a) and 3-11-(b), gives us an understanding that no appreciable difference can be seen in essential nature of crack growth in both high and low strength steels. The QC crack first appears in the crack growth process in both high and low strength steel specimens. This QC mode continues to grow up to the transition point where the growth mode changes into IG mode with the unstable growth in high strength steel specimen, while in low strength steel specimen, no transition to IG crack seems to be appeared in the crack growth process.

According to the forementioned evidence, it can be concluded that the susceptibility to delayed fracture is related to the fact that high susceptibility prefers the IG crack growth triggered by the QC crack resulting in a brittle fracture, while no IG crack appears in the low susceptibility condition. Therefore, we examined the mechanistic factors, which must have an influence on the development of the QC crack and the IG crack in the delayed fracture.

3-3-2 Influence of the mechanistic factor on the development of IG crack

3-3-2-1 Relationship between the crack tip configuration and IG crack development

QC cracks in low strength steels under hydrogen attack show a mode of crack growth different from that in high strength steels. The fractographic analysis revealed that the QC crack in low strength steels grows without changing the mode of growth into IG crack which is the characteristics of high strength steels, but QC crack grows with a coalescence of a number of neighboring QC cracks under a relatively long period of time followed by a development of MVC leading to final fracture. The QC cracks should remain as non-propagating crack (NPC) when the applied stress is not enough to boost the crack coalescence. From the mechanistic viewpoint, a possible reason for the QC crack to propagate or to remain as NPC is a role of plasticity at the crack tip, namely, the crack tip blunting. If a blunting is involved at the crack tip in low strength steels, the hydrogen diffusion and concentration may be disturbed to a certain extent [24] compared with high strength steels which keeps a sharp crack tip configuration with little plastic deformation. This may reduce the stress intensity together with the reduced hydrogen accumulation at the crack tip resulting in difficulty of the IG crack growing from the QC crack front. A question arises as to whether the crack tip blunting actually behaves as we expected. To examine the relationship between the level of yield strength and the morphology of the initiated crack tip in steels, two kinds of specimens were prepared for the metallographic observations of the cross section: one was ASTM A490 steel with a higher yield strength of 1344MPa and the other was API X65 steel with a lower yield strength of 709MPa.

A configuration of the tip of QC crack was then examined on steels which had

already been loaded for 10^4 minutes to produce QC crack in the specimen under sustained load at the stress level of 90MPa for ASTM A490 steel and 500MPa for API X65 steel, both of which correspond to the respective threshold stress of the delayed fracture with hydrogen charging condition of 500A/m^2 . After 10^4 minutes from the start of loading and hydrogen charging, sustained load tests were discontinued and the metallurgical examination on the cross section of the gauge section of specimen was made after mechanical polishing and metallographical treatments to see the crack tip configuration as shown in Fig. 3-12.

Figure 3-12-(a) and (b) shows the micrographs of subsurface crack tip, which were observed in the cross section by using optical microscope. These results showed two types of different crack tip morphologies of the initial cracks of QC developed in the two specimens tested. The one crack tip is very sharp with no appreciable plasticity in ASTM A490 steel having high yield strength. On the other hand, in the case of API X65 steel having a low yield strength, the crack tip showed an appreciable plastic deformation both at the tip and the flank of the crack as shown in Fig. 3-12-(a) and (b) respectively. From this evidence, the reason for the difficulty for the onset of IG crack growth from the QC crack in the low strength steel may be explained that the crack tip blunting is easily built up in the low strength steel compared with the high strength steel and this may suppress the hydrogen accumulation near the crack tip resulting in disappearance of IG crack growth which should be triggered by the QC crack in the crack growth process.

3-3-2-2 Relationship between the crack tip blunting and IG crack development in high strength steels

To examine whether or not the above explanation for low strength steels can be acceptable for other structural steels as to any amount of blunting is possible at the crack tip, the high strength steel specimens having QC cracks, the tip of which is difficult to blunt under ordinary condition for delayed fracture, were prepared by the forementioned loading procedure. If the additional crack tip blunting is applied for the QC crack in high strength steels, it is expected that the crack growth behavior would be different from that having a sharp crack tip where the QC crack easily propagates into IG mode resulting in premature fracture. However, preparations of QC crack having plastic blunting at the crack tip in high strength steels is difficult to accomplish in a specimen since the QC crack develops in the invisible subsurface of the specimen. There seems to be no way to identify a particular QC crack leading to fatal fracture of the specimen among other embedded QC cracks and to catch the plastic blunting at the crack tip. Therefore, an influence of the crack tip blunting behavior on the onset of IG crack growth from the QC crack was estimated from the available evidence of the surface fatigue crack behavior instead of the embedded QC crack in the specimen.

Hence, surface fatigue pre-cracked specimens were prepared in place of the specimen having subsurface QC cracks. We arranged the experiment using the ASTM A490 steel specimen having the surface fatigue pre-crack of 250 μ m in depth with the loading cycles about $N=10^4$ - 10^5 under the cyclic stress amplitude of 400MPa. These fatigue pre-cracked specimens were further loaded to make a blunted crack tip under the stress condition as follows: Loading conditions were selected as 45% ($\sigma=605$ MPa) and 90% ($\sigma=1210$ MPa) of the yield strength with the strain rate of 10^{-5} /s.

Employing these specimens, the sustained load test was carried out at 400MPa after hydrogen charging for 24 hours at the current density of 500A/m² under no applied

stress. Fractography showed that the critical crack eventually started at the fatigue pre-crack and that the mode of the crack growth was still intergranular even in the case of the specimen, which was pre-loaded up to 90% of the yield strength level. However, the length of the IG crack facet in front of the fatigue pre-crack obviously reduced compared with the specimen having no additional crack tip blunting.

The relationship between the IG crack length and the normalized applied stress for blunting with respect to the yield strength is given in Fig. 3-13. The IG crack length decreased with increasing magnitude of normalized applied stress. Since the magnitude of this stress must be related to the degree of plastic blunting at the crack tip, it can be suggested from Fig. 3-13 together with the evidence shown in Fig. 3-12 that the crack tip blunting has a definite influence on the condition for the onset of growth of IG crack from the fatigue pre-crack front. The detailed mechanisms of IG crack development from the QC crack in an unnotched specimen under hydrogen attack is not fully understood, but it must be related to the sharpness or bluntness of the morphology of QC crack tip which should influence the behavior of hydrogen diffusion and accumulation capability [25-26] during the crack propagation process.

3-3-2-3 Relationship between the tempering temperature and IG crack development

The following experiments were carried out to obtain a further understanding of the influence of the reduction in the yield strength on the behavior of IG crack development from the tip of the fatigue pre-crack. Fatigue pre-cracked specimens of ASTM A490 steel were prepared to have reduced yield strengths by the forementioned higher tempering temperature process. They were tempered at 473K, 673K and 973K

for 1 hour in vacuum furnace (1.3×10^{-4} Pa) respectively, and then hydrogen charged for 24 hours at a current density of 2000 A/m^2 with no applied stress to keep up the state of original crack tip morphology of fatigue pre-crack. These specimens were subsequently subjected to a delayed fracture test under 400 MPa at the same hydrogen environment.

Figure 3-14 shows the relationship between the facet lengths of IG cracks from the crack front of the fatigue pre-crack and the tempering temperature. Both specimens tempered at 473K and 673K showed the same crack propagation behavior accompanying IG crack, and the length of IG facet remarkably decreased with increase in the tempering temperature from 473K to 673K, and all traces of IG crack facet eventually disappeared off from the pre-crack front of the particular specimen tempered at 973K as shown in Fig. 3-14. Accordingly, the activation of the onset of IG crack growth in the fracture process under hydrogen attack depends mostly on the yielding resistance of the specimen which is directly related to the crack tip blunting and the crack tip stress state for the concentration and diffusion of hydrogen.

3-3-3 Mechanisms of QC crack development to delayed fracture in steels

From the results of fractographic analyses of the subsurface crack propagation under hydrogen attack and of the study on the mechanisms of delayed fracture with respect to the various levels of yield strength of steels, we may reach a comprehensive understanding of the crack development behavior under hydrogen environment as shown in Table 3-3. This table summarizes the forementioned results of crack propagation analyses in a simple model. It is obvious that the initial crack is always the QC crack irrespective of the strength level of the specimens. It is evident that the basic

manner of crack growth process consists of the QC crack, IG crack, and MVC in the delayed fracture of various kinds of structural steels. However, in the case of low strength steels, the IG cracking process may disappear due to the crack tip blunting resulting in difficulty of the hydrogen concentration.

Since the fracture appearance in the delayed fracture shows various features in response to the level of yield strength of steels, many of the previous results [42] have pointed that the fracture mechanisms of delayed fracture should be understood as a different phenomenon depending on the level of yield strength. Then, the feature of crack growth at initial stage of fracture in low strength steels was always identified as the transgranular crack differing from that of high strength steel in which the IG crack was common especially when the specimen had a sharp notch. On the contrary, if the model of the sequence of crack growth “QC→IG→MVC” is considered as essential for the crack propagation mechanism regardless of the level of yield strength in steels under the delayed fracture process as shown in this experiment using the unnotched specimen, a susceptibility to the delayed fracture is directly related to the condition for an appearance of the IG crack growth which can be explained by the blunting of the QC crack tip.

3-4 Summary

A mechanistic aspect of the susceptibility to delayed fracture of structural steel was studied with an emphasis on the subsurface crack development mechanisms using various types of steels which have yield strength levels ranging from 500MPa to 1400MPa. Results obtained are summarized in the followings:

(1) The susceptibility to the delayed fracture increases with an increase in the yield strength level irrespective of the variety of steels.

(2) The delayed fracture strength remarkably decreases at a particular strength level about $\sigma_y=1000\text{MPa}$ in ASTM A490 and S35C steels. The development of the subsurface QC crack is common and fundamental phenomenon to high and low strength steels under hydrogen attack.

(3) SEM examination of the fracture surface revealed that two types of crack propagation morphologies exist in delayed fracture of steels: one is $\text{QC} \rightarrow \text{IG} \rightarrow \text{MVC}$ in high strength steels and the other is $\text{QC} \rightarrow \text{MVC}$ in low strength steels. It can be explained that the IG crack is absent in the case of low strength steels in which the coalescence of micro-QC cracks occurs leading to the final fracture accompanying MVC growth.

(4) On the basis of mechanistic viewpoint, a magnitude of the susceptibility to delayed fracture in steels can be explained from the degree of crack tip blunting due to the magnitude of yield strength.

Chapter 4

Crack initiation mechanisms at welded joints under hydrogen attack

Abstract

To avoid the fracture of welded joints, “over-matching” has been employed as a useful and practical method in welding operation. This has been known as an effective approach to maintain a high static strength level of the welded structure. However, it is also known that welded joints have a high susceptibility to delayed fracture under hydrogen attack. To examine the mechanisms of delayed fracture of welded joints that consist of the weld metal and the base metal of API X80 steel, sustained load tests were carried out under hydrogen attack using four types of unnotched specimens; the specimen A which consists of three microstructural elements-- a base metal, a heat affect zone (HAZ), and a weld metal; the specimens B and C are composed of a single microstructure-- a base metal and a weld metal respectively, and the specimen D is composed of a single weld microstructure without marked defects due to welding operation. Although the weld metal at welded joints has a yield strength level below 900MPa, it shows almost the same tendency toward hydrogen susceptibility as that of the high strength steels having the yield strength level above 1200MPa. Weld defects such as blowholes can be responsible for the high susceptibility to hydrogen embrittlement of welded joints.

Key Words: Weld Metal, Initiation crack, Susceptibility, Yield stress, Threshold stress, Quasi-Cleavage Crack

4-1 Introduction

To prevent welded joints from fracture, “over-matching” has been applied as a useful method for welding operation of the joints of pipelines. This brings about higher strength at welded joints compared with the base metal under static applied load in the case of present pipeline steel API X100 [133]. Although over-matching operation

is an effective welding method and is popular for providing tough structures to pipeline systems in power plants, high sensitivity of the welded joints to hydrogen cracking is a crucial problem for welding process of pipeline steels especially in high pressure and aggressive environments.

When hydrogen penetrates into a specimen and accumulates at the interface of the non-metallic inclusions and the matrix, a significant amount of cracking may occur even in low and medium strength alloy steels such as the API X series commonly used for pipelines and pressure vessels in oil and chemical industries [138]. It is reported that the elongated MnS inclusion is the most favorable site for the initiation of hydrogen induced cracking (HIC) [139-140]. This type of hydrogen damage is also called hydrogen induced blistering cracking or stepwise cracking, which is accelerated by the effect of band structure of the specimen [141-142]. Many studies so far have been carried out to develop various improved grades of pipeline steels with low susceptibility to delayed fracture under aggressive environments [143], but it has been reported that the API X60 up to X80 types of pipeline steels are prone to hydrogen induced cracking even in the absence of applied stresses [144].

On the other hand, the initial crack nucleation and growth mechanisms of hydrogen embrittlement (HE) of welded structures have attracted little attention of researchers so far. Therefore, an aim of the study in this chapter is to elucidate the mechanisms of crack development in the weld metal and the base metal under hydrogen attack. To examine the fracture mechanisms of the base metal of API X80 steel and the weld metal, conventional delayed fracture tests were carried out using specially prepared specimens as shown in the next chapter.

4-2 Experimental procedure

The material employed in this study was an API X80 steel plate having a thickness of 17.5mm, chemical compositions of which are given in Table 4-1. The API X80 steel plate was welded using welding wire with chemical compositions as shown in Table 4-1. In this study, MAG welding method was employed using argon and carbon dioxide as primary shielding gases. The welding condition is summarized as shown in Table 4-2. From this welded plate, the type A specimen, which consists of three microstructural components, the base metal, the HAZ and the weld metal, was machined into an hourglass shape with a gauge length of 25mm and with a mid-section diameter of 5mm for the sustained load test. Details of the welded plate and the shape and dimensions of this unnotched specimen are illustrated schematically in Fig. 4-1.

For evaluations of the susceptibility to delayed fracture of the base metal and the weld metal, specimens B and C, each of which is composed of a single microstructural component of a base metal and a weld metal respectively, were also prepared from the same welded plate and machined into an unnotched specimen with a gauge length of 10mm, and with a mid-section diameter of 5mm. To examine the delayed fracture strength of the weld metal without marked defects due to welding operation, the specimen D was prepared through vacuum plasma melting to achieve defect-free weld metal specimens. The specimen D was arranged from an ingot with $270 \times 60 \times 15 \text{ mm}^3$ and machined into an unnotched specimen with a gauge length of 10mm, and with a mid-section diameter of 5mm. Details of the shape and dimensions of the specimens B, C and D are illustrated in Fig. 4-2. The mechanical properties of the specimens B, C and D are shown in Table 4-3.

These specimens were mechanically polished, and were subsequently hydrogen

charged cathodically through the surface using a platinum anode in 0.03mol H_2SO_4 solution with a current density of 500A/m^2 and at ambient temperature. The rest of the specimen surface was covered with shielding tape to prevent the specimen surface from H_2SO_4 attack. Conventional delayed fracture tests were carried out using a 3-ton creep-testing machine under conditions in which mechanical loading began simultaneously with hydrogen charging, and both 0.03mol concentration of H_2SO_4 and 500A/m^2 current density were kept constant during the test to the moment of final fracture, as shown in Fig. 4-3. A feature of crack propagation on the fracture surface was then traced using a scanning electron microscope (SEM).

4-3 Results and Discussion

4-3-1 Feature of microstructures at the welded joints

Figure 4-4 shows micrographs of the cross section of the welded plate specimen. From these, the base metal was shown to be a mixture of ferrite and pearlite structures with a segregation band, and the HAZ was also found to be a mixture of fine grained ferrite and pearlite structures as shown in Fig. 4-4-(a), and (b). Optical micrograph of the weld metal consists primarily of acicular ferrite (AF), Widmanstaetten ferrite (WF), and grain boundary ferrite (GF) microstructures. Figure 4-4-(c) gives an example showing the mixed feature of AF, WF, GF and pearlite microstructures in the weld metal. The weld metal without marked defects was also shown to be a mixture feature of AF, WF and GF microstructures as shown in Fig. 4-4-(d). However, weld defects such as blowholes due to welding operation were hardly detected by means of optical microstructural examination in the weld metal microstructure.

4-3-2 Delayed fracture characteristics of welded joints

Figure 4-5 shows the relationship between fracture stress and time to fracture under hydrogen attack for the specimen A. Although both the base metal and the weld metal have low strength levels ranging from 610MPa~860MPa, their fracture behavior seems to be similar to those of high strength steels such as ASTM A490 and S35C steels which were heat treated to the strength level above 1200MPa. It is notable that the delayed fracture has occurred even at extremely low stress level such as 100MPa, as recognized in Fig.4-5.

Welded joints are composed of three microstructural components in series connection-- the base metal, the HAZ, and the weld metal, each of which has a different mechanical property, as shown in Table 4-3. If the weakest-link-concept, that was first proposed by Peirce F.T. in 1926 [145], is applied to the fracture event of welded joints in air, the weakest spot can be the base metal not the weld metal, as shown in Fig. 4-6-(b), since welded joints are usually prepared under the concept of “over-matching”. To examine the role of the weakest spot in welded joints under delayed fracture, an identification of the fracture spot at the welded joints in specimen A was carefully made on all the fractured specimens given in Fig. 4-5. Possible fracture spots are categorized into three microstructural constituents; base metal, HAZ, and weld metal, respectively.

Figure 4-7 shows the results of the categorization of the fracture spot in the welded joints of specimen A. In the case of stress levels above 600MPa, close to the yield strength of the base metal, the fracture spot was found in the base metal in this delayed fracture tests. On the other hand, in the case of low applied stress where the applied stress was less than 600MPa, the delayed fracture occurred in the weld metal, with few exception of the case of HAZ region fracture, which occurred at 550MPa. Although the weld metal has a higher static strength than the base metal, i.e.,

“over-matching”, as shown in Table 4-3, the fracture prefers to the weld metal as the weakest spot in delayed fracture instead of the base metal.

Consequently, the hydrogen degradation at welded joints can be understood as a phenomenon that the fatal crack prefers to develop at the weld metal damaged due to the thermal history during welding operation. Although the fracture curve of specimen A given in Fig. 4-5 seems to be a result of simple delayed fracture, the result of Fig. 4-7 evidently implies that not one but two types of fracture mechanisms are dominating the embrittlement fracture of the welded joints subjected to hydrogen attack. Multiple mechanisms for crack development dominate the fracture of welded joints; one in higher strength levels and the other in lower strength levels. This implies that it is insufficient to understand the essential fracture characteristics of welded joints from the forementioned simple result of delayed fracture of the specimen A. To have a comprehensive understanding of the nature of the susceptibility of the base metal and the weld metal to delayed fracture under hydrogen attack, both of the specimen B representing base metal and the specimen C representing weld metal are subjected to a sustained load fracture test, the results of which are given in the next chapter.

4-3-3 Difference in susceptibility to delayed fracture between the base metal and the weld metal

Figure 4-8 shows the relationship between fracture stress and time to fracture for both specimens B (base metal) and C (weld metal) under hydrogen attack. Since the overall fracture strength of specimen is dependent on the strength of the weakest spot in microstructure, it can be expected that the fracture strength of specimen A should be closely related to the strength of either specimen B or C. The results of Fig. 4-8 clearly show that the base metal specimen has a higher level of threshold stress for hydrogen

attack than the weld metal specimen. Since the intrinsic strength level of the weld metal is comparable to that of ordinary low strength steels, it is reasonable to expect the weld metal to show high resistance for delayed fracture. However, the results are quite different from expectations. This extremely low strength level of weld metal in the figure is comparable to the case of high strength steels. The threshold stress (σ_{th}) was then determined as the largest value of the applied stress at which fracture did not occur, after the elapsed time period of 10^4 minutes. The threshold stress of the weld metal was considerably lower than that of the base metal even though the yield strength of both metals stays in a similar range of yield strength. Furthermore, this result clearly shows a fact that delayed fracture under hydrogen attack occurs even at extremely low stress level such as 200MPa.

Figure 4-9 shows a schematic illustration of the superposition of the two fracture curves of the base and weld metals, both of which are microstructural constituents connected serially in the specimen A. On the basis of this consideration, the fracture behavior of the specimen A can be explained from the superimposed fracture curve. In the range of relatively higher stress levels and shorter elapsed time period before remarkable decrease in fracture strength, the delayed fracture strength of welded joints is dominated mainly by the fracture strength of the base metal. On the other hand, in the range of lower applied stress level and longer elapsed time period, the delayed fracture strength of welded joints is determined predominantly by the fracture strength of the weld metal. The thick single solid line represents the expected fracture curves of the specimen A composed of a combination of two fracture curves. Thus, the results of delayed fracture tests of the specimen A were plotted against this expected curve given in Fig. 4-9. Figure 4-10 shows a quite good agreement between the two results.

To have a general understanding of the susceptibility to the delayed fracture of the individual specimens of B and C, the levels of the threshold stresses of each specimen were compared with the results of the quenched and tempered carbon steel specimens having yield strength levels ranging from 500MPa~1400MPa as shown in Fig. 4-11. The threshold stress of delayed fracture was evaluated by using the yield strength normalized as the ratio of the threshold stress to the yield strength (σ_{th}/σ_y). It is found from Fig. 4-11 that the normalized delayed fracture strength of the specimen B (base metal) has the same level as those of low strength steels, while the delayed fracture strength of the specimen C (weld metal) remains in an extremely low level comparable to the high strength steels having the yield strength above 1200MPa. This may raise a question as to why the weld metal shows higher susceptibility than that of the base metal though their strength levels are in the same range.

Since a feature of crack initiation and propagation can be related to the susceptibility to delayed fracture, the characteristic of crack growth morphologies in both base and weld metals and the details of fracture surface were carefully observed in the next chapter by fractographic analysis with SEM.

4-3-4 Difference in crack propagation mechanisms between the base metal and the weld metal

Figure 4-12 shows schematic illustrations of the morphologies of crack propagation and SEM photographs of the QC and IG cracks in the specimens B and C. The sequence of the crack propagation modes in the base metal can be traced in the particular order of QC→MVC as shown in Fig. 4-12-(a). Initial QC cracks develop accompanying coalescence of the QC cracks to reach the critical length at which they trigger an unstable crack growth with the MVC mode. Although there was no

appreciable difference in the level of yield strength between the specimen B and the specimen C, the crack propagation mechanisms of the weld metal shows different characteristics from the base metal as shown in Fig. 4-12-(b). The sequence of crack propagation mode in the weld metal is in the order of QC→IG→MVC. It is noticeable that the crack propagation mode following the initial QC crack is not MVC but IG crack in the case of the weld metal as shown in Fig. 4-12-(b). This evidence coincides with the suggestion from the previous studies [83] indicating that the appearance of the IG crack mode in the crack propagation period of the weld metal is one of the important factors of the high susceptibility to delayed fracture.

It is interesting to know that the nucleation sites of the initial crack in the base metal and the weld metal are different from each other, even though the initial crack modes are identically QC cracks. To examine the initiation sites of the origin of QC cracks in the base metal and the weld metal, the fracture surface of the specimens B and C were carefully examined. Most of the initial cracks in the specimen B started at the non-metallic inclusions as shown in Fig. 4-13-(a). On the other hand, most of the initiation sites of QC cracks in the specimen C were the blowholes as shown in Fig. 4-13-(b). In addition, particular attention should be given to the numbers of blowholes and non-metallic inclusions at initiation sites that give useful information on how the QC cracks develop and propagate in the base and weld metals under hydrogen attack. To evaluate the numbers of blowholes in the weld metal and non-metallic inclusions in the base metal, the fracture surface of the specimens B and C were carefully examined through SEM micrographs. Figure 4-14 shows the numbers of blowholes and non-metallic inclusions observed as nucleation sites of QC cracks on fracture surface. The number of blowholes and non-metallic inclusions which became initiation sites for

QC cracks in the weld metal were approximately 4 times larger than the number of non-metallic inclusions which also played the nucleation sites in the development of QC cracks in base metal. It is noted from this result that the blowholes in weld metal have an important role on the degradation of delayed fracture strength in welded metal.

4-3-5 Role of blowholes in weld metal under hydrogen attack

A question arises as to whether or not the weld metal itself before welding has a high susceptibility to delayed fracture. Then, a particular specimen D was arranged from the ingot of welding wire as mentioned in the experimental procedure. Presently there seems to be no way to prepare welded joints without having welding defects due to welding operation. From the results of the fracture behavior of the specimen D, it can be presumed that welding defects such as blowholes in weld metal influences on susceptibility to delayed fracture. Since the strength level of the specimen D having the yield strength of 531MPa is comparable to ordinary low strength steels, it is expected to show a relatively low susceptibility to delayed fracture, i.e., a higher delayed fracture strength. Figure 4-15 shows the relationship between the fracture stress and the time to fracture for the specimen D together with the results of the specimen C given by the solid line without data plots. The specimen D has a higher threshold stress than the specimen C as shown in Fig. 4-15. To compare the susceptibility to hydrogen embrittlement between the specimen C (weld metal) and the weld metal without marked welding defects such as blowholes, the susceptibility to delayed fracture of the specimen D was also evaluated by the ratio, σ_{th} / σ_y , in a similar manner shown in Fig. 4-11. Figure 4-11 shows that the normalized delayed fracture strength of the specimen D has a higher strength level than the weld metal. The level of susceptibility to delayed fracture can be influenced by the feature of crack development behavior in the

microstructure. To compare the difference in susceptibility between the weld metal (specimen C) and the weld metal without marked welding defects such as blowholes (specimen D), the details of crack propagation morphologies on the fracture surface of both specimens were examined by fractographic analysis with SEM. Figure 4-16 shows the schematic illustration of the morphology of crack propagation, SEM photographs of QC cracks, and the initial sites of QC cracks on the fracture surface of the specimen D. In case of the specimen D, the initial crack mode is basically QC with a mixture mode of QC crack and cleavage crack. The sequence of the crack propagation process is in the particular order of QC→MVC as shown in Fig. 4-16-(a). The initial QC cracks develop accompanying also coalescence with each other to reach the critical length at which they trigger an unstable crack growth with the MVC mode as the base metal and the weld metal. To examine the initiation sites of the QC cracks in the weld metal without marked welding defects such as blowholes, the fracture surface of the specimen D was carefully examined. The initial sites of the QC cracks in the specimen D started at the non-metallic inclusions as shown in Fig. 4-16-(b). The evidence that the crack in the specimen D initiates at the non-metallic inclusion not at the blowhole may suggest the most probable reason for the low susceptibility to delayed fracture of specimen D compared to the results of weld metal.

Although the effects of welding defects such as blowholes on mechanical properties are dependent on their size, shape, number, and distribution [146-147], the weld metal has a higher mechanical property in air than the base metal due to the effect of “over-matching” described in Table 4-3. When the specimen A is subjected to a sustained load test in air, not in an aggressive environment, the fracture should start at the base metal if we accept the weakest-link-concept. In this case the defects such as

blowholes in the weld metal may not act as the weakest spot so that the static fracture does not occur at the weld metal. On the other hand, when the specimen A is subjected to sustained load tests where the applied stress is a relatively low stress level under hydrogen attack, the fracture starts from the weld metal not from the base metal. It is considered that welding defects, such as blowholes, may significantly affect on reduction in fracture strength of the weld metal under hydrogen attack. It is reported that the blowholes in the vicinity of the specimen surface in A 5183 weld metal become a fatigue crack initiation site due to stress concentration effect, but if the blowholes are located far from the surface of the specimen, they do not become a fatigue crack initiation site in air [148] showing almost no appreciable effects on fatigue properties. On the other hand, when the welded joints of API X80 steel were subjected to sustained load tests under hydrogen attack, most of the blowholes in the weld metal gave initiation sites of QC cracks irrespective of the distance from the surface of the specimen. From these experimental results, it is noted that the blowholes which became initiation sites in development of QC cracks in crack propagation, provide the most susceptible site as preexisting defects in the weld metal and play an important role to promote the progress of hydrogen accumulation and to develop a critical subsurface crack due to hydrogen attack.

4-4 Summary

The susceptibility to delayed fracture and the mechanisms of hydrogen related fracture in a welded plate were studied using four types of unnotched specimens which were specially prepared with an emphasis on the initial crack development behavior.

Results obtained are summarized as follows:

(1) The weld metal shows a tendency to increase susceptibility to delayed fracture in a similar manner as crack development in the high strength steels with yield strength above 1200MPa level.

(2) Even though the weld metal has a high performance in mechanical properties compared to that of the base metal in air, the fracture occurs from the weld metal not from the base metal of welded joints under hydrogen attack. The welding defects such as blowholes are associated to increase the susceptibility to delayed fracture in the weld metal.

(3) On the basis of the weakest-link-concept, the delayed fracture behavior of welded joints can be explained from the two superimposed delayed fracture curves of the base and weld metals: the delayed fracture strength of the welded joints at higher stress levels is dominated by the base metal, while at lower stress levels it is dominated by the weld metal.

(4) The morphology of initial cracks in welded joints is always Quasi-Cleavage irrespective of the difference in trigger defects, i.e., blowholes or non-metallic inclusions. This may give us a generalized aspect of the fracture morphology of structural steels under hydrogen attack where the development of crack involves the typical Quasi-Cleavage followed by Inter-Granular or Micro-Void Coalescence.

Chapter 5

Conclusions and Further work

5-1 Conclusions

In this study, mechanistic aspects of the mechanisms of subsurface crack propagation and hydrogen degradation in high and low strength steels with various magnitudes of yield strength ranging from 500MPa to 1400MPa were studied with special attention on specimen shape and dimensions. The mechanisms of critical crack development and susceptibility to delayed fracture in welded joints of API X80 steel were also studied. The following conclusions were obtained.

(1) Mechanistic aspects of the development of critical crack in thin specimens of high strength steels under hydrogen attack (Chapter 2)

To examine the influence of the localized stress condition introduced by the difference in specimen shape and thickness on the development of critical crack, and on the delayed fracture time associated with hydrogen diffusion and accumulation at the vicinity of the subsurface crack tip, delayed fracture tests were carried out using three types of unnotched specimens. Even though the plate thickness of thin plate specimen and the wall thickness of thin walled hollow specimen become extremely thin up to 0.3mm, the initial QC crack still develops in the subsurface of specimens. Although there is no essential difference in the morphology of crack propagation between the thick and the thin specimens, the time-to-fracture depends on the thickness of specimens regardless of specimen shape in steels. This implies that the development of the initial

hydrogen crack is still under the influence of local stress condition though no appreciable difference in stress condition is observed in macroscopically very thin specimen.

(2) Mechanistic aspects of hydrogen degradation in high and low strength steels (Chapter 3)

A mechanistic aspect of the susceptibility to delayed fracture of steels was studied with an emphasis on the critical behavior of QC crack and IG crack development using various levels of yield strength steels ranging from 500MPa to 1400MPa. The susceptibility to delayed fracture increases with increasing yield strength irrespective of steels. The delayed fracture strength remarkably decreases at a particular strength level beyond $\sigma_y=1000\text{MPa}$ in ASTM A490 and S35C steels. SEM examination of the fracture surface revealed that two types of crack propagation morphologies exist in steels: one is QC→IG→MVC in high strength steels and the other is QC→MVC in low strength steels. This implies that the IG crack mode is absent in case of low strength steels in which coalescence of micro-QC cracks occurs leading to final fracture accompanying MVC growth. This explanation is supported by the plastic deformation at the crack tip due to low yield strength. It is further suggested from the experimental results that the blunting of crack tip can be also responsible for the absence of IG crack from an initial crack in the crack growth process and the low susceptibility to delayed fracture in low strength steels. The morphology of initial cracks in the high and low strength levels is always Quasi-Cleavage irrespective of the levels of the yield strength and the initial crack tip blunting. This may give us a generalized aspect of fracture morphology of structural steels under hydrogen attack where the development of crack involves the typical Quasi-Cleavage followed by Inter-Granular or Micro-Void coalescence.

(3) Mechanisms of critical crack development at welded joints under hydrogen attack (Chapter 4)

To examine influence of the mechanisms of crack propagation on the susceptibility to delayed fracture at welded joints, sustained load tests were carried out using welded plates which consisted of the weld metal, the HAZ, and the base metal of API X80 steel. Since an intrinsic strengths of the base and weld metals is not so different compared to the low strength steels having the yield strength below 900MPa, it is not unreasonable to expect low susceptibility to delayed fracture. However, the weld metal shows almost the same tendency of susceptibility to delayed fracture as that of the high strength steels having the yield strength above 1200MPa. Although blowholes are present as an inevitable defect in the weld metal, when the weld metal was subjected to tensile tests in air, the blowholes did not act as the weakest point to promote crack propagation. When the weld metal was subjected to sustained load tests under hydrogen attack, however, the blowholes became an initiation site of critical crack development in crack propagation. The reason for the high susceptibility to delayed fracture of the weld metal compared to the base metal can be explained from the experimental evidence that the weld defects such as blowholes are the most susceptible sites and provide an initiation site of QC cracks development in the crack propagation process under hydrogen attack. On the basis of the weakest-link-concept, the delayed fracture behavior of welded joints can be explained from the two superimposed delayed fracture curves of the base and weld metals: the delayed fracture strength of welded joints at higher stress levels is dominated by the base metal, while at lower stress levels it is dominated by the weld metal.

From the fractographic analysis of crack propagation using SEM in the fracture

surface of unnotched specimen, it is found that the feature of initial crack mode is not IG crack but QC crack irrespective of the shape and dimensions of specimens, and of the levels of yield strength in steels. The essential elements of morphologies in crack propagation under hydrogen attack are composed of three modes: QC crack, IG crack, and MVC. The development of QC crack as an initial and critical crack is a common and fundamental phenomenon in high and low strength steels under hydrogen attack. When the unstable crack mode of IG crack can easily transfer from the stable crack mode of QC crack in crack propagation process, it means that the susceptibility to delayed fracture is high and the fracture strength drops to extremely low levels, e.g., less than 1/10 of the yield strength. The following crack mode next to the QC crack depends on various parameters such as the degree of blunting at the crack tip due to the magnitudes of yield strength, preexisting defects like blowholes in the welded joints, the hydrogen diffusion and accumulation ability which is affected by the microstructures, and stress conditions around the critical crack tip.

5-2 Further work

Since the mechanisms of crack development and propagation due to the combination of hydrogen diffusion and stress concentration in local region such as defects or non-metallic inclusions are very complicated, no single mechanisms can explain the degradation of fracture strength in steels under hydrogen attack. In this study attention is focused on the influence of mechanistic aspects on the feature of initial crack development and the susceptibility to delayed fracture. There still lies considerable scope of further progress toward a comprehensive understanding of

hydrogen behavior related to the mechanisms of delayed fracture in steels. Hence some recommendations for future studies are given in the followings:

(1) Clarity about the role of hydrogen in nucleation and growth of critical cracks in steels is especially important to have a comprehensive understanding of the development mechanisms of subsurface crack such as the QC and TG cracks under hydrogen attack. Details of examination are needed to understand the influence of microstructures of steels on the early stage of crack development under hydrogen attack. It is also recommended to study the critical matter between the actual fracture problems and the basic understanding of crack development such as QC crack in delayed fracture.

(2) A study on the development of QC crack is proposed as an essential and fundamental phenomenon in unnotched specimens under hydrogen attack through the technique of fractographic analysis on fracture surface, especially within the sustained load test. Thus the concept of initial QC crack should be modified and developed by extending the range of test parameters such as in the high and low cycle fatigue situations.

Acknowledgements

This dissertation was carried out at the school of Fundamental Science and Technology, Keio University under direction and guidance of Professor Kunihiro Yamada of Keio University. I would like to express greatest appreciation to Professor Kunihiro Yamada for his guidance, warm encouragement and reviewing of the present dissertation.

I am deeply indebted to many people who helped with this work. I would like to express my gratitude to Professor Masao Shimizu, Takahiko Kunoh, Yasuo Suga, Testuya Suzuki, for their valuable advices and review. I would like to acknowledge numerous individuals who have contributed to my research on welded weldment, Dr. Naoto Hagiwara, Mr. Hiroyuki Motohashi and Mr. Hiroshi Yatabe of TOKYO GAS Co., LTD. for their invaluable comments and discussions on the welded plates. I would like to thank Dr. Abraham T. Kim and Miss. Dana Purdy for their English proofreading.

I am very grateful to all members in the laboratory of Keio University for their encouragement and cooperation. In particular, I am deeply grateful Mr. Shunsuke Yamada, Mr. Daisaku Hirayama, Mr. Shuzi Nishiyama, Yoshiaki Hiromatsu, Mr. Yasuyuki Moriyama, Mr. Shinitsi Mannen, Mr. Hiroyuki Kosimizu, Mr. Yuki Komatsuzaki, Mr. Osamu Hatano, and Mr. Kazuhiko Matano for their discussions, advice and assistance.

Finally, I thank so much for God those who help us and wish to express my thanks to my wife and little children for their love, hearty encouragement and support.

2004.12.

Haengsik JOO

List of References

- (1) Fujita, T. and Yamada, Y., SCC and HE of iron base alloys, NACE-5, 1977, p.36.
- (2) H.K. Birnbaum, in: Z.A. Foroulis (Ed.), Environment-Sensitive Fracture of Engineering Materials, TMS-AIME, 1977, p.326.
- (3) J. P. Hirth and H. H. Johnson, Corrosion, 32, 1976, p.3.
- (4) T. Tabata, H.K. Birnbaum, Scripta Metall., Vol. 17, 1983, p.947.
- (5) M. M. Mulholland, E. S. Ege, T. A. Khraishi, M. F. Horstemeyer and Y. -L. Shen, Materials Science and Engineering A, Vol. 360, Issues 1-2, 2003, p.160.
- (6) O. Durand-Drouhin, A. E. Santana, A. Karimi, V. H. Derflinger and A. Schütze, Surface and Coatings Technology, Vol. 163-164, 2003, p.260.
- (7) A. R. Troiano, Trans. Met. SOC, AIME, Vol. 218, 1960, p.832.
- (8) K. Ip, M. E. Overberg, Y. W. Heo, D. P. Norton, S. J. Pearton, C. E. Stutz, S. O. Kucheyev, C. Jagadish, J. S. Williams, B. Luo, F. Ren, D. C. Look and J. M. Zavada, Solid-State Electronics, Vol. 47, Issue 12, 2003, p.2255.
- (9) Y. Kimura, Y. Sakai, T. Hara, A. Belyakov and K. Tsuzaki, Scripta Materialia, Vol. 49, Issue 11, 2003, p.1111.
- (10) A. Zielinski and P. Domzalicki, Journal of Materials Processing Technology, Vol. 133, Issues 1-2, 2003, p.230.
- (11) M. Hayakawa, S. Matsuoka, K. Tsuzaki, H. Hanada and M. Sugisaki, Scripta Materialia, Vol. 47, Issue 10, 2002, p.6555.
- (12) C. L. Mgmahon, Metal. Trans., Vol. 9A-5, 1978, p.625.
- (13) R. M. Horn, Metal, Trans., Vol. 9A, 1978, p.1039.
- (14) P. Cotterill, The hydrogen embrittlement of metals, London, pergamon press, Prog. in Metersials Science, Vol. 9, Issue 4, 1961, p.205.
- (15) H. K. Birnbaum, C. Buckley, F. Zeides, E. Sirois, P. Rozenak, S. Spooner and J. S. Lin, Journal of Alloys and Compounds, Vol. 253-254, 1997, p.260.
- (16) B. G. Pound, Acta. Mater., Vol. 46, 1998, p.5733.
- (17) Y. Kimura, Y. Sakai, T. Hara, A. Belyakov and K. Tsuzaki, Scripta Materialia, Vol.49, Issue 11, 2003, p.1111.
- (18) A. H. M. Krom, H. J. Maier, R. W. J. Koers and A. Bakker, Materials Science and Engineering A, Vol. 271, 1999, p.22.
- (19) Liufa Liu, Akio Hirose and Kojiro F. Kobayashi, Acta Materialia, 2, 2002, p.1331.
- (20) A. H. M. Krom, R. W. J. Koers and A. Bakker, Journal of the Mechanics and Physics of Solids, 25, 1999, p.971.
- (21) P. Sofronis and J. Lufrano, Materials Science and Engineering A, Vol. 260,

- Issues 1-2, 1999, p.41.
- (22) Shinji Konosu and Tsuyoshi Nakaniwa, Engineering Failure Analysis, Vol. 5, Issue 4, 1998, p.323.
 - (23) J. Lufrano, P. Sofronis and H. K. Birnbaum, Journal of the Mechanics and Physics of Solids, Vol. 46, Issue 9, 1998, p.1497.
 - (24) J. Lufrano, P. Sofronis and D. Symons, Engineering Fracture Mechanics, Vol. 59, Issue 6, 1998, p.827.
 - (25) J. Lufrano and P. Sofronis, Acta Materialia, Vol. 46, Issue 5, 1998, p.1519.
 - (26) A. H. M. Krom, A. Bakker and R. W. J. Koers, International Journal of Pressure Vessels and Piping, Vol. 72, Issue 2, 1997, p.139.
 - (27) J. Lufrano, P. Sofronis and H. K. Birnbaum, Journal of the Mechanics and Physics of Solids, Vol. 44, Issue 2, 1996, p.179.
 - (28) A. Taha and P. Sofronis. Eng. Fract. Mech. Vol. 68, 2001, p. 803.
 - (29) Y. Liang, P. Sofronis and R. H. Dodds, Jr., Materials Science and Engineering A, Vol. 366, Issue 2, 2004, p.397.
 - (30) “Advances in Delayed Fracture Solution”, The Iron and Steel Institute of Japan, 1997, p.1.
 - (31) J. Völkl and G. Alefeld, Ref. 18, p.816.
 - (32) C. D. Beachem: Mt. Trans., Vol. 3, 1972, p.437.
 - (33) I. M. Bernstein and A. Q. Thompson: Int. Met. Rev., vol. 21, 1976, p.269.
 - (34) H. Kimura and H. Matsui: scr. Met., vol. 13, 1979, p.221.
 - (35) A. M. Adair and R. E. Hook: Acta Met., vol. 10, 1962, p.741.
 - (36) S. Asano, T. Sugimoto, and N. Ohtani: Bull. Nagoya Inst. Tech., vol. 25, 1973, p.361.
 - (37) R. A. Oriani: Stress corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, NACE-5, NACE, Houston, TX, 1977, p. 351.
 - (38) N. N. Petch: Phil. Mag., vol. 1, 1956, p.331.
 - (39) C. Zapffe and C. Sims: Trans. AIME, vol. 145, 1941, p.225.
 - (40) R. M. Latanision and H. Opperhause, Jr.: Hydrogen in Metals, ASM, Metals Park, OH, 1974, p. 539.
 - (41) J. J. Gilman: Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, NACE-5, NACE, Houston, TX, 1977, p. 326-331.
 - (42) J. P. Hirth, Metall. Trans., 11A, 1980, p.881.
 - (43) C. A. Zapfee, J. Iron steel Inst., vol. 154, 1946, p.123.
 - (44) R. P. Frohberg, W. J. Barnet and A. R. Troiano, Trans. ASM, vol. 47, 1955, p.892.

- (45) P. Bastien and P. Azou, *compt. Rend. Acad. Sci.*, vol. 232, 1951, p.1845.
- (46) P. G. Bastien, *Physical Metallurgy of stress corrosion Fracture*, New York, Inter-science Pub. Inc., 1959, p.311.
- (47) J. Plusquellec, P. Azou and P. G. Bastien, *ibid*, vol. 244, 1957, p.1195.
- (48) J. Bastien and P. Azou, *Compt. Rend. Acad. Sci.*, vol. 232, 1951, p.1845.
- (49) S. V. Nair and J. K. Tien, *Met. Trans.*, 16A, No. 12, 1985, p.2333.
- (50) M. R. Louthan, Jr., *Hydrogen in metals.*, ASM, 1974, p.53.
- (51) M. R. Louthan, G. R. Caskey, J. A. Donovan and D. E. Rawl, *Mater. Sci. Eng.*, vol. 10, 1972, p.357.
- (52) P. Sofronis and R.M. McMeeking *J. Mech. Phys. Solids* 37, 1989, p.317.
- (53) A.H.M. Krom, R.W.J. Koers and A. Bakker *J. Mech. Phys. Solids* 47, 1999, p.971.
- (54) G. Sandoz, *metallurg, Trans. Vol. 3(5)*, 1972, p.1169.
- (55) R. P. Gangloff, *Mater. Sci. and Engng*, A103, 1988, p.157.
- (56) J.P. Thomas and R.P. Wei *Mater. Sci. Eng. A159*, 1992, p.205.
- (57) K.A. Esakul and W.W. Gerberich *Scripta Metall.* 17, 1983, p.1079.
- (58) W. Dietzel and M. Pfuff In: A.W. Thompson and N.R. Moody, Editors, *Hydrogen Effects in Materials*, TMS, Warrendale, PA, 1996, p.303.
- (59) R.S. Piascik and R.P. Gangloff In: A.W. Thompson and N.R. Moody, Editors, *Hydrogen Effects in Materials*, TMS, Warrendale, PA, 1996, p.409.
- (60) C. ST. John and W. W. Gerberich, *Metall. Trans.*, Vol. 4, 1973, p.589.
- (61) W. W. Gerberich and Y. T. Chen, *Metall. Trans.*, Vol. 6A, 1975, p.271.
- (62) W.W. Gerberich, P.G. Marsh and J.W. Hoehn In: A.W. Thompson and N.R. Moody, Editors, *Hydrogen Effects in Materials*, TMS, Warrendale, PA, 1996, p.539.
- (63) N.R. Moody, M.W. Perra and S.L. Robinson In: N.R. Moody and A.W. Thompson, Editors, *Hydrogen Effects on Material Behavior*, TMS, Warrendale, PA, 1990, p.625.
- (64) Y. Yamaguchi, H. Nonaka and K. Yamakawa *Corrosion* 53, 1997, p.147.
- (65) W. W. Gerberich and Y. T. Chen, *Metallurgical Transactions A*, Vol. A, 1975, p.271.
- (66) I. Chattoraj, M. Tarafder, Swapan K. Das and S.Tarafder, *Materials Science and Engineering A*, vol. 339, Issues 1-2, 2 January 2003, p.136.
- (67) Mitshshi OYANAGI, Tetsuya SUAUKI and Kunihiro YAMADA, *J. Soc. Mat. SCI., Japan*, Vol. 51, 2002, p.561.
- (68) S. Murata, 'Fractographpic', 2000, Tokyo, Maruzen Company, Limited (in

- Japanese).
- (69) W. W. Gerberich and Y. T. chen, Metal. Trans., 6A, 1975, p.271.
 - (70) M. F. Stevens and I. M. Berenstein, Metal. Trans., 20A, 1989, p.909.
 - (71) S. M. Bruemmer, R. H. Jones, M. T. Thomas and D. R. Baer, Metall. Trans., Vol. 14A, 1983, p.233.
 - (72) G.M. Pressouyre, R. Blondeau, G. Primon, L. Cadiou, Very low inclusion and impurity content steels as a solution to resist sour environments, in: C.G. Interrante, G.M. Pressouyre (Eds.), Current Solutions to Hydrogen Problems in Steels, Proceedings of the First International Conference, ASM, Ohio, 1982, p.212.
 - (73) I. Chattoraj, S. B. Tiwari, A. K. Ray, A. Mitra and S. K. Das, Corrosion Science, Vol. 37, Issue 6, 1995, p.885.
 - (74) G. Domizzi, G. Anteri and J. Ovejero-García, Corrosion Science, Vol. 43, 2001, p.325.
 - (75) C. Manfredi and J. L. Otegui, Engineering Failure Analysis, Vol. 9, 2002, p.495.
 - (76) L. W. Tsay, W. C. Lee, R. K. Shiue and J. K. Wu, Corrosion Science, Vol. 44, 2002, p.2101.
 - (77) A. Vrostkova and B. Stefan, Metall. Mater. 28, 1990, p.426.
 - (78) I.O. Shim and J.G. Byrne Mat. Sci. Eng. A-Struct. A 123, 1990, p.169.
 - (79) H. Asahi, A. Yagi and M. Ueno ISIJ Int., 33, 1993, p.1190.
 - (80) Ingolfur Thorbjörnsson, Materials & Design, Vol. 16, 1995, p.97.
 - (81) T. Zhang, W. Y. Chu, K. W. Gao and L. J. Qiao, Materials Science and Engineering A, Vol. 347, Issues 1-2, 2003, p.291.
 - (82) P. Sofronis and J. Lufrano Materials Science and Engineering A, Vol. 260, Issues 1-2, 1999, p.41.
 - (83) Y. Nakatani, H. Matsuoka and K. Yamada, fracture from Defects (Ed. M. W. Brown, E. R. de los Rios and K. J. Miller), 3, 1998, p.1121.
 - (84) Laymond, L., "Hydrogen Embrittlement: Prevention and Control", Philadelphia, ASTM STP 962, 1988, p.10.
 - (85) J.P.Hirth, Metall. Trans., 11A, 1980, p.861.
 - (86) K.kiuchi and R.B.McLellan, Acta Metall., 31, 1983, p.961.
 - (87) T. Yokobri, Jr., T. Nemoto, K. Sato and T. Yamada, Trans. Jpn, Soc. Mech. Eng., A 59, 1993, p. 2120.
 - (88) M. F. Stevens, I.M. Bernstein., Metall. Trans., 20A, 1989, p.909.
 - (89) S.I. Pyun, H.K. Lee, Metall. Trans., 21A, 1990, p.2577.
 - (90) A. Taha, P. Sofronis, Engineering Fracture Mechanics, Vol.68, 2001, p.803.

- (91) C.P. Wu, L.W. Tsay, C. Chen, Mater. Sci. and Engin., A346, 2003, p.302.
- (92) K. Tsuboi, H. Yatabe and K. Yamada, Science and Technology (The Institute of Materials), 12, 1966, p.400.
- (93) H. Yatabe, K. Yamada, E. R. de los Rios and K. J. Miller, Fatigue & Fracture of engineering Materials & structure, 18, 1995, p.377.
- (94) Y. Nakatani, T. Higashi and K. Yamada, Fatigue & Fracture of Engineering Materials & structure, 22, 1999, p.393.
- (95) H. Yatabe and K. Yamada, The Proc. 13th European Conference on Fracture in CD-ROM, 2000.
- (96) T. Ninakuchi, K. Yamada and T. Kunio, Transactions of the Japan Society of Mechanical Engineers, Vol. 59, 1992, p.304. (in Japanese)
- (97) T. Ninakuchi, K. Yamada and T. Kunio, Trans. Jpn, Soc. Mech. Eng., 56, A, 1990, p.114.
- (98) K. Tshboi and k. Yamada, Trans. Jpn, Soc. Mech. Eng., 60, A, 1994, p.1157.
- (99) K. Tsuboi, H. Yatabe and K. Yamada, Mater. Sci. and Tech., 12, 1996, p.400.
- (100) T. Kimura and K. Yamada, Trans. Jpn, Soc. Mech. Eng., 58, A, 1992, p.78.
- (101) Y. Nakatani and K. Yamada, Trans. Jpn, Soc. Mech. Eng., 63, A, 1997, p.1392.
- (102) M. Ishikawa, Y. Nakatani and K. Yamada, "Hydrogen Transport and Cracking in Metals", the institutes of Materials, 1995, p.95
- (103) Y. Nakatani, K. Utsubo, K. Yamada, Trans. Jpn, Soc. Mech. Eng., 64, A, 1998, p.2561.
- (104) A. S. Tetelman and W. D. Robertson, Trans AIME, Vol. 224, 1962, p.775.
- (105) Y. Murakami, M. Ishida, Trans. Jpn, Soc. Mech. Eng., 51A, 1985, p.1050.
- (106) Y. Murakami, S. Kodama, S. Onuma, Trans. Jpn, Soc. Mech. Eng., 54A, 1988, p.688.
- (107) Ishikawa, M., Nakatani, Y. and Yamada, K., Hydrogne transport and cracking in metals, The Institute of materials, 1995, p.95.
- (108) Minakuchi, T., Yamada, K. and Kunio, T., Trans. Japan Soc. Mech. Eng. 56(A), (522), 1990, p.304.
- (109) Matsuyama, S. Delayed fracture. Nikkan kogyo Shimbun, 1989, p.8. (in Japanese)
- (110) Beachem, C.D Metall Trans. 3, 1972, p.437.
- (111) J. K. Chakravartty, G. E. Prasad, T. K. Sinha and M. K. Asundi, Journal of Nuclear Materials, Vol. 138, Issue 1, 1986, p.107.
- (112) Omar A. El kebir and Andrzej Szummer, International Journal of Hydrogen Energy, Vol.27, Issues 7-8, 2002, p.793.

- (113) Kazuyuki Kaneko, Ken'ichi Yokoyama, Keiji Moriyama, Kenzo Asaoka, Jun'ichi Sakai and Michihiko Nagumo, *Biomaterials*, Vol.24, Issue 12, 2003, p.2113.
- (114) L. W. Tsay, Z. W. Lin, R. K. Shiue and C. Chen, *Materials Science and Engineering A*, Vol.290, Issues 1-2, 2000, p.46.
- (115) J. G. Cowie, L. J. Lowder, R. J. Culbertson and W. E. KosikR. Brown, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, Vol.59-60, Part 2, 1991, p.871.
- (116) Fujita, T. and Yamada, Y., SCC and HE of iron base alloys, *NACE-5*, 1977, P.736.
- (117) Ikeda, A. and Terasaki, F. High pressure technology, (*Atsuryoku-Gizyutsu*) Vol.16, 1978, p. 16.
- (118) Paredes, F. and Mize, W. W. *Oil and Gas J.*, Vol.54, 1954, p. 99.
- (119) Class, T. *Proc. Second int. conger. Metallic Corrosion*, 1963, p.342, (NACE).
- (120) Naumann, F. K. and Spies, F. *Praktische Metallographie*, Vol.10, 1973, p.475.
- (121) Irving, R.R. *Iron Age*, June, Vol.24, 1974, p.8.
- (122) C. Manfredi and J. L. Otegui, *Engineering Failure Analysis*, Vol.9, Issue 5, 2002, p. 495.
- (123) J. V. Sharp, J. Billingham and M. J. Robinson, *Marine Structures*, Vol. 14, Issues 4-5, 2001, p. 537.
- (124) I. Chattoraj, S. B. Tiwari, A. K. Ray, A. Mitra and S. K. Das, *Corrosion Science*, Vol.37, Issue 6, 1995, p. 885.
- (125) J. L. Albarran, L. Martinez and H. F. Lopez, *Corrosion Science*, Vol.41, Issue 6, 1999, p.1037.
- (126) G. Domizzi, G. Anteri and J. Ovejero-García, *Corrosion Science*, Vol.43, Issue 2, 2001, p. 325.
- (127) A. Vyrostkova and B. Stefan *Metall. Mater.* 28, 1990, p. 426.
- (128) L. W. Tsay, W. C. Lee, R. K. Shiue and J. K. Wu, *Corrosion Science*, Vol.44, Issue 9, 2002, p. 2101.
- (129) H. Asahi, A. Yagi and M. Ueno *ISIJ Int.* 33, 1993, p. 1190.
- (130) A. Taha and P. Sofronis, *Engineering Fracture Mechanics*, Vol.68, Issue 6, 2001, p. 803.
- (131) P. Sofronis and J. Lufrano, *Materials Science and Engineering A*, Vol.260, Issues 1-2, 1999, p. 41.
- (132) Ingolfur Thorbjörnsson, *Materials & Design*, Vol.16, Issue 2, 1995, p. 97.
- (133) J. H. Bulloch, *Theoretical and Applied Fracture Mechanics*, Vol.21, Issue 2,

- 1994, p.143.
- (134) T. Zhang, W. Y. Chu, K. W. Gao and L. J. Qiao and L. J. Qiao, Materials Science and Engineering A, Vol.347, Issues 1-2, 2003, p.291.
- (135) Jarmila Woodtli and Rolf Kieselbach, Engineering Failure Analysis, Vol.7, Issue 6, 2000, p. 427.
- (136) R. N. Parkins, Materials Characterization, Vol. 26, 1991, p. 303.
- (137) H. Qiu and Y. Kawaguchi, Materials Science and Engineering A, Vol. 348, Issues 1-2, 2003, p. 22
- (138) G. M. Pressouyre, R. Blondeau, G. Primon, L. Cadiou. Very low inclusion and impurity content steels as a solution to resist sour environments, in C. G. Interrante, G. M. Pressouyre (Eds), current solutions to hydrogen problems in steels, proceeding of the first international conference, ASM, Ohio, 1982, p.212.
- (139) T. Taira, K. Tsukada, Y. Kobayashi, H. Inagaki, T. Watanabe, Corrosion, Vol. 37(1), 1981, p.5.
- (140) EM. Moore, JJ. Warga, Mat. Perf., Vol. 15(6), 1976, p.17.
- (141) M. Kowaka, F. Ferasaki, S. Nagata and A. Ikeda, Res. Rep. 14 Sumitomo Metal Industries, 1975, p.36.
- (142) S. A. Golovaneko, Alloys for the 80s, Ann Arbor, MI, june 17-18, 1980, p. 20.
- (143) H. Huang, W. J. D. Shaw, Corrosion Science, 34, 1993, p.61.
- (144) H. Margot-Marette, G. Bardou, J. C. Charbonnere, Corrosion Science, 27, 1987, p.1009.
- (145) Peirce F. T., Journal of the textile institute, Vol. 17, 1926, p.355.
- (146) Kammer P.A., Randall M.D., Monroe R.E., Groth W.G., Weld J. Res Suppl, Vol. 42, 1963, p.433.
- (147) Shore R.J. Mccauley R.B., Weld J. Res Suppl, Vol.49, 1970, p.311.
- (148) Tetsumi Yuri, Toshio Ogata, Masahiro Saito, Yoshiaki Hirayama, Cryogenics, Vol. 41, 2001, p.475.

List of publications

Original papers

- (1) Haengsik JOO, Kunihiro Yamada, [Mechanistic aspects of delayed fracture of thin plate and thin walled hollow specimen subjected to sustained loading.], Transaction of the Japan Society of mechanical engineers, Vol. 688, No-69, 2003, p. 1717-1722. (in Japanese)
- (2) Haengsik JOO, Kunihiro Yamada, [Mechanistic aspects of the hydrogen crack growth in delayed fracture of structural steels], Journal of material testing research association of Japan (Accepted: in Japanese)

List of presentations

- (1) Haengsik JOO, Kunihiro Yamada, [Critical growth of Subsurface Cracks in High Strength Steel Subjected to Hydrogen Attack], Proceedings of the second international conference on steel & composite structures (ICSCS'04), 2004, Organized by KAIST p.193.
- (2) Osamu Hatano, Daisaku Hirayama, Haengsik JOO and Kunihiro Yamada, [Fatigue cracks propagation behavior originating at internal crack result from hydrogen attack], Proceedings of the 2004 Annual Meeting of the JSME/MMD, 2004, p.323-324.
- (3) Haengsik JOO, Kunihiro Yamada, [Relationship between the susceptibility to delayed fracture behavior and crack propagation of high and low strength steel in hydrogen environment], Proceedings of the 2003 Annual Meeting of the JSME/MMD, 2003, p.803-804.
- (4) Shuji Nishiyama, Shunsuke Yamada, Haengsik JOO and Kunihiro Yamada, [A study on the delayed fracture of high strength steel welds in hydrogen environment], Proceedings of the 2003 Annual Meeting of the JSME/MMD, 2003, p.805-806.

- (5) Haengsik JOO, Kunihiro Yamada. [Mechanistic aspects of delayed fracture of thin high strength hollow specimen], Proceedings of the 2002 Annual Meeting of the JSME/MMD, 2002, p.725-726.
- (6) Haengsik JOO, Kunihiro Yamada, [Mechanistic aspects of delayed fracture of thin high strength plate subjected to sustained loading], Mechanical Engineering Congress, 2002 Japan (MECJ-02), p.297-298.

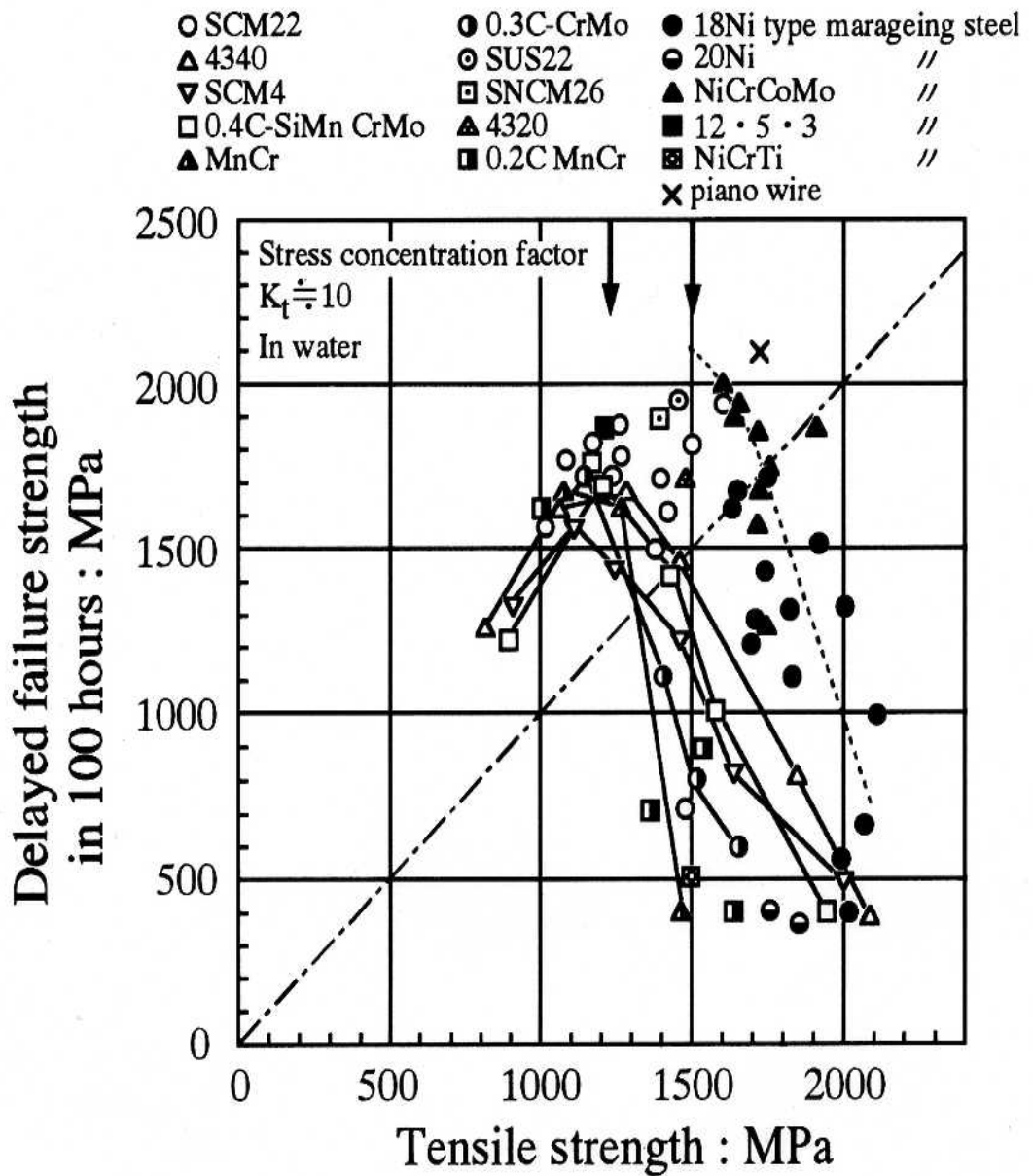
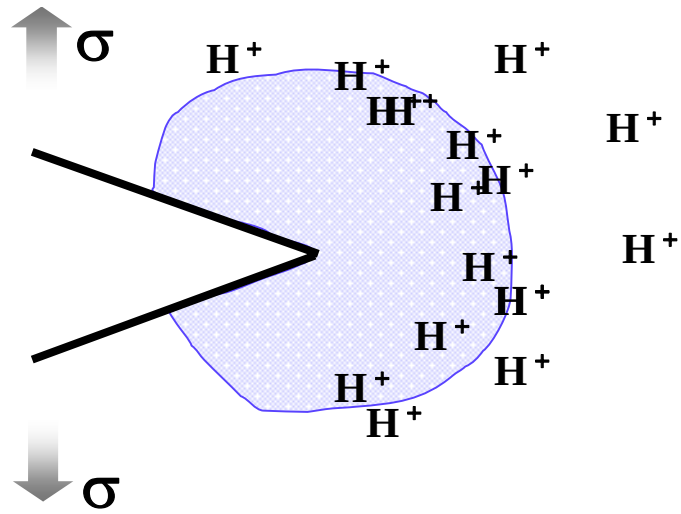


Fig. 1-1. High strength steels have high susceptibility to hydrogen cracking resulting in extremely low fracture stress levels (Notched specimen) [1].



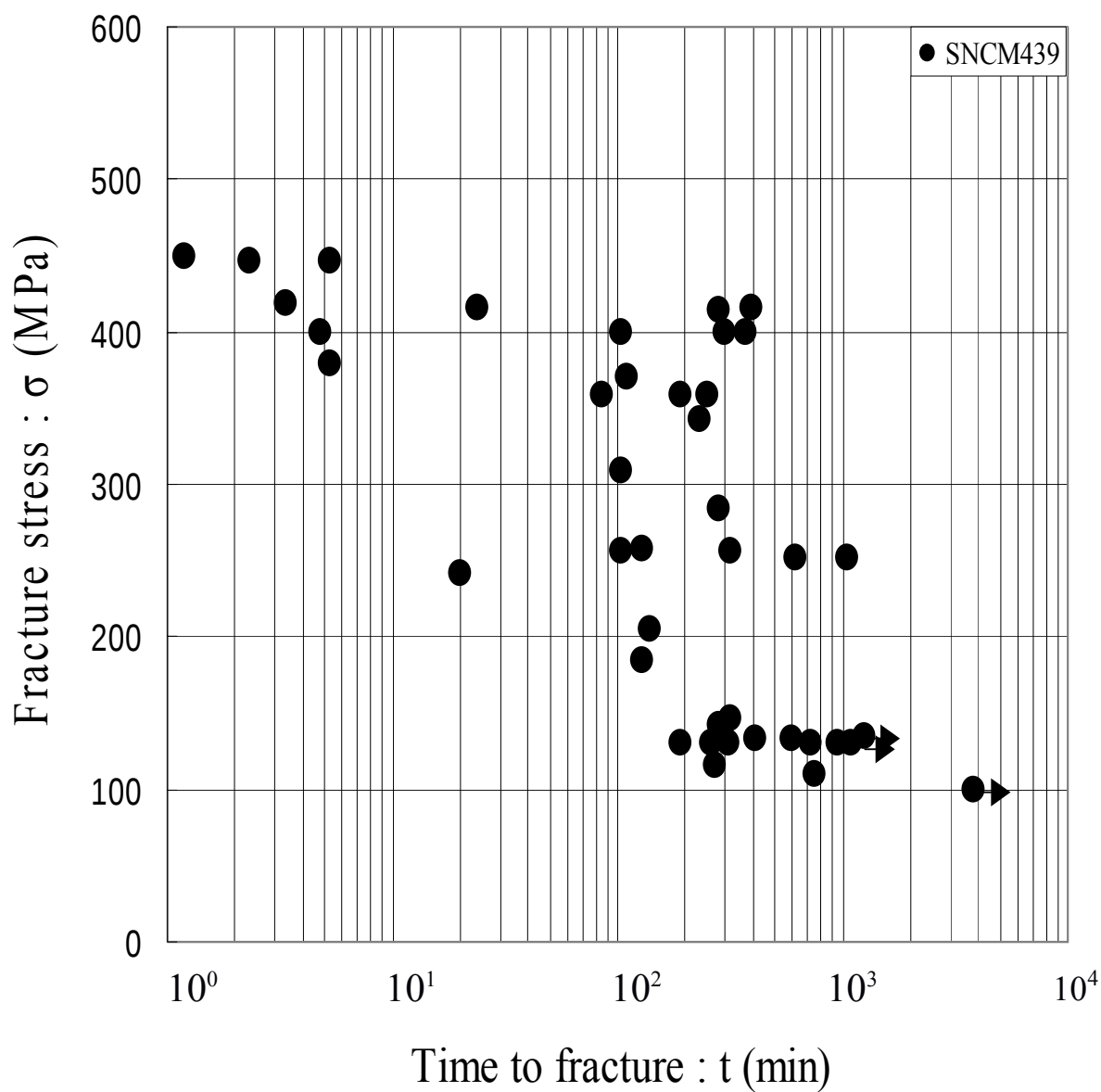
Crack tip of notched specimen

Fig. 1-2. Schematic illustration for interactions of stress concentration and hydrogen accumulation in front of the crack that leads to delayed fracture.

Table 2-1. Chemical compositions of specimens

wt%

Materials	C	Si	Mn	P	S	Cr	Mo	Fe
ASTM-A490	0.33	0.16	0.68	0.016	0.01	0.79	0.16	Bal
S35C (AISI 1035)	0.36	0.24	0.75	0.1	0.15	0.11	—	Bal



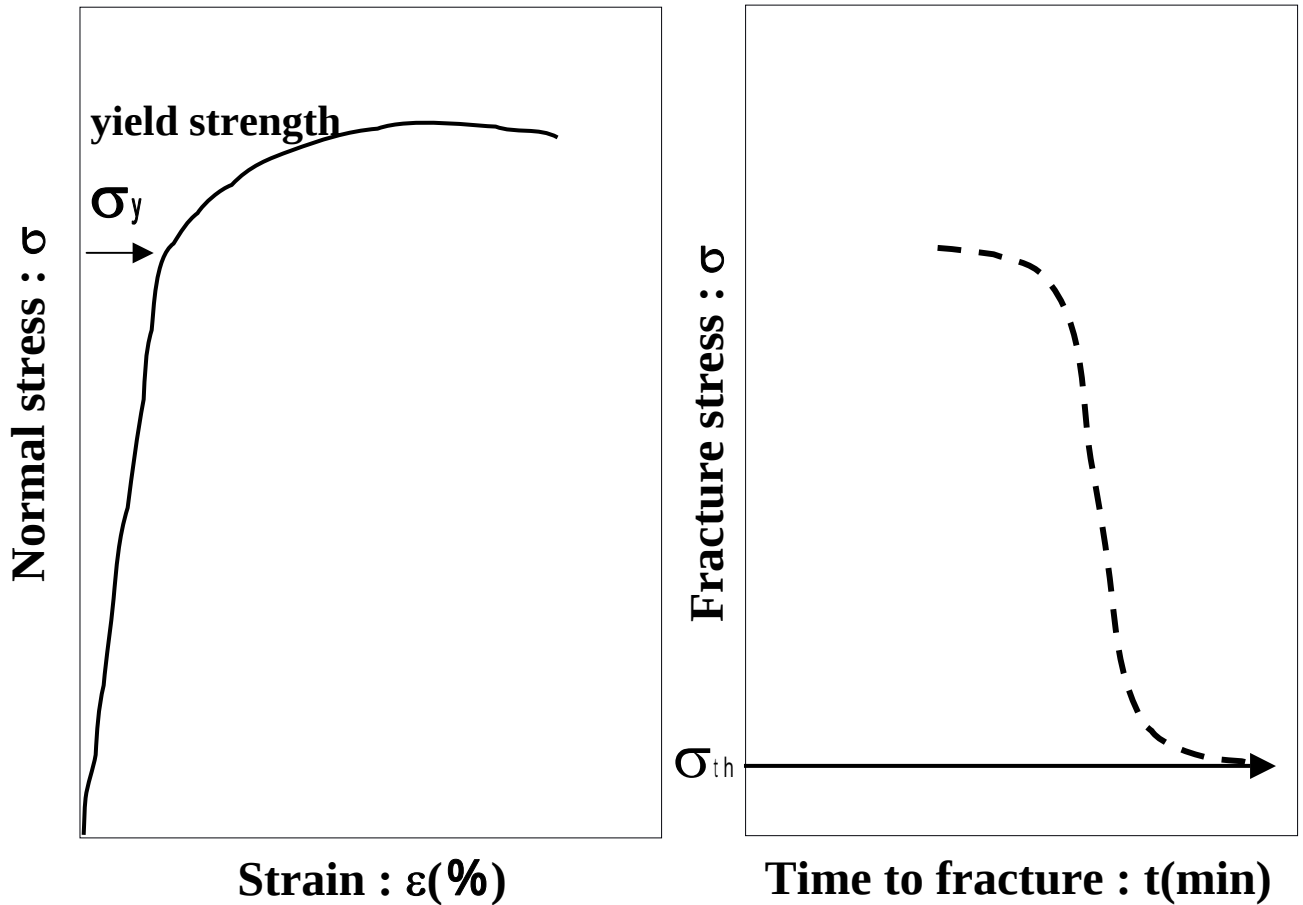
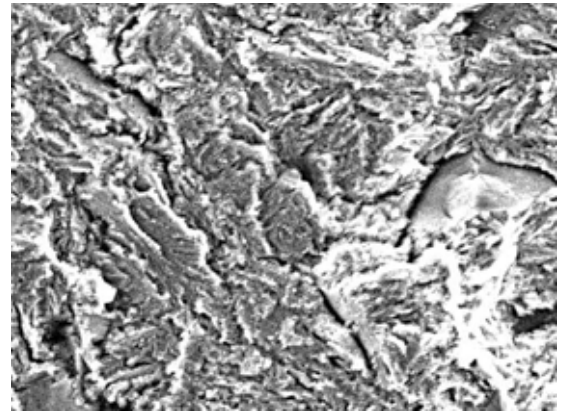
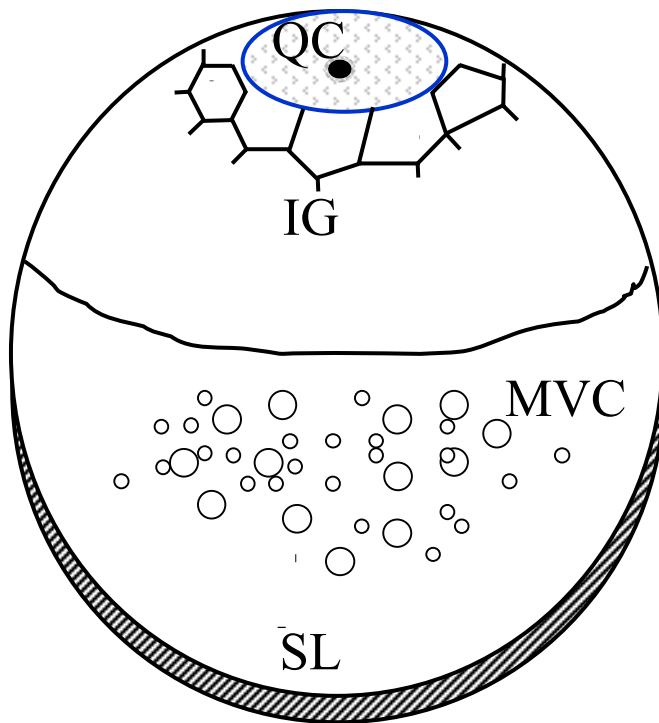
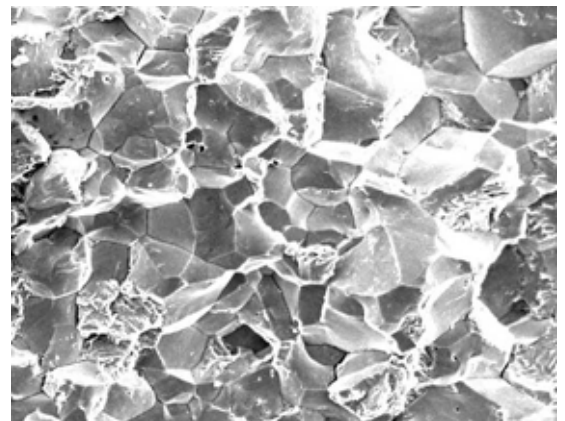


Fig. 2-2. High strength steel has a high susceptibility to hydrogen cracking at extremely low stress levels, about 1/10 level of the yield strength, leading to brittle fracture known as Delayed Fracture.

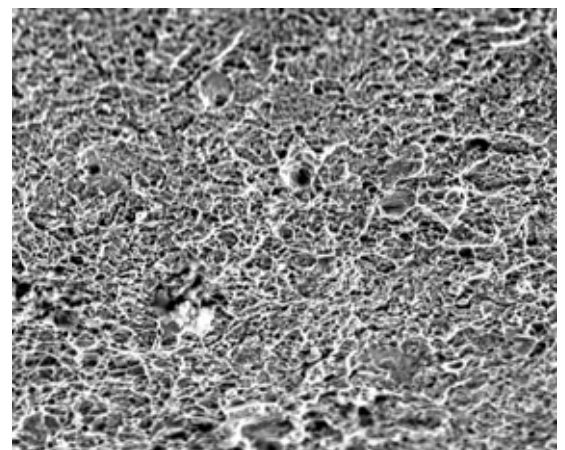
QC : Quasi-cleavage
 IG : Inter-granular
 MVC : Micro-void coalescence



QC facet



IG facet



MVC facet

Fig. 2-3. SEM fractographs and morphological characteristics of the fracture surface of unnotched solid specimen subjected to delayed fracture test.

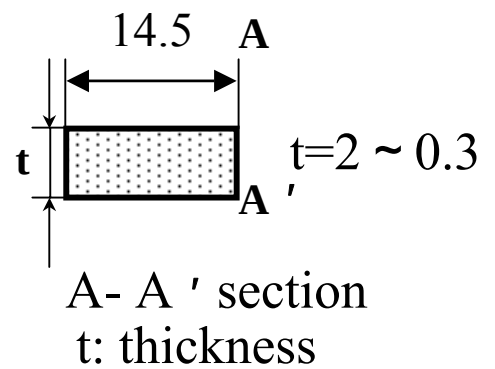
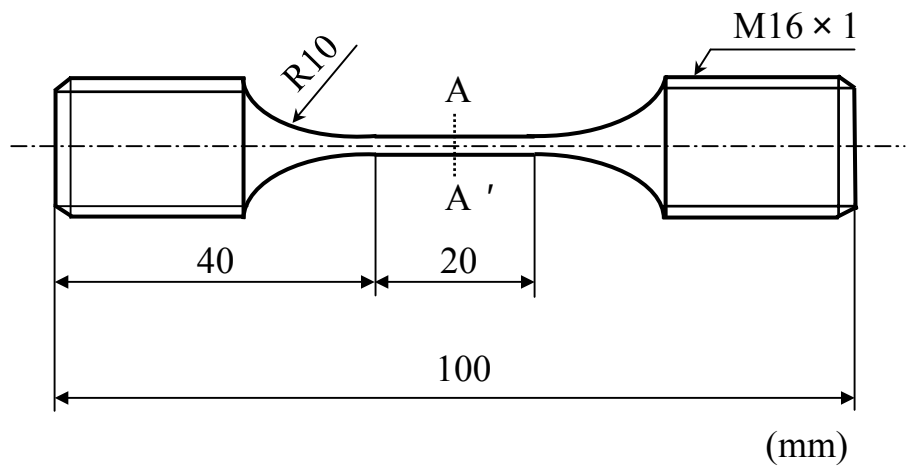
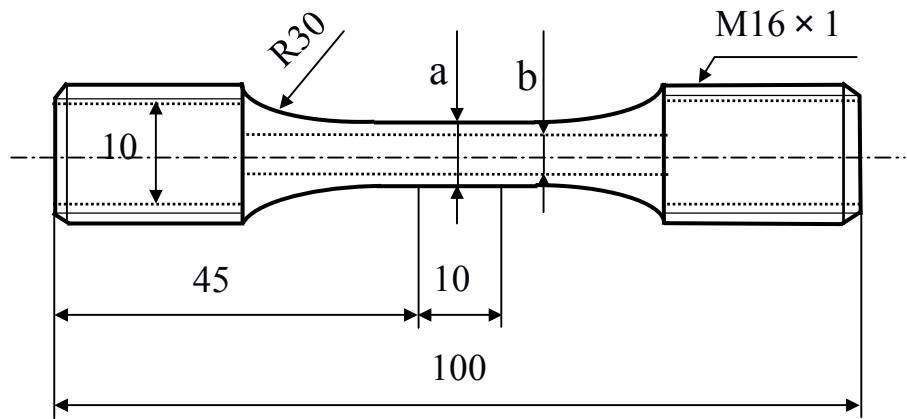


Fig. 2-4-(a). Shape and dimensions of thin plate specimens of ASTM A490 steel.



(mm)

Thickness	a	b
8	8	0
2	8	4
0.3	8	7.4

Fig. 2-4-(b). Shape and dimensions of thin walled hollow and solid specimens of S35C steel.

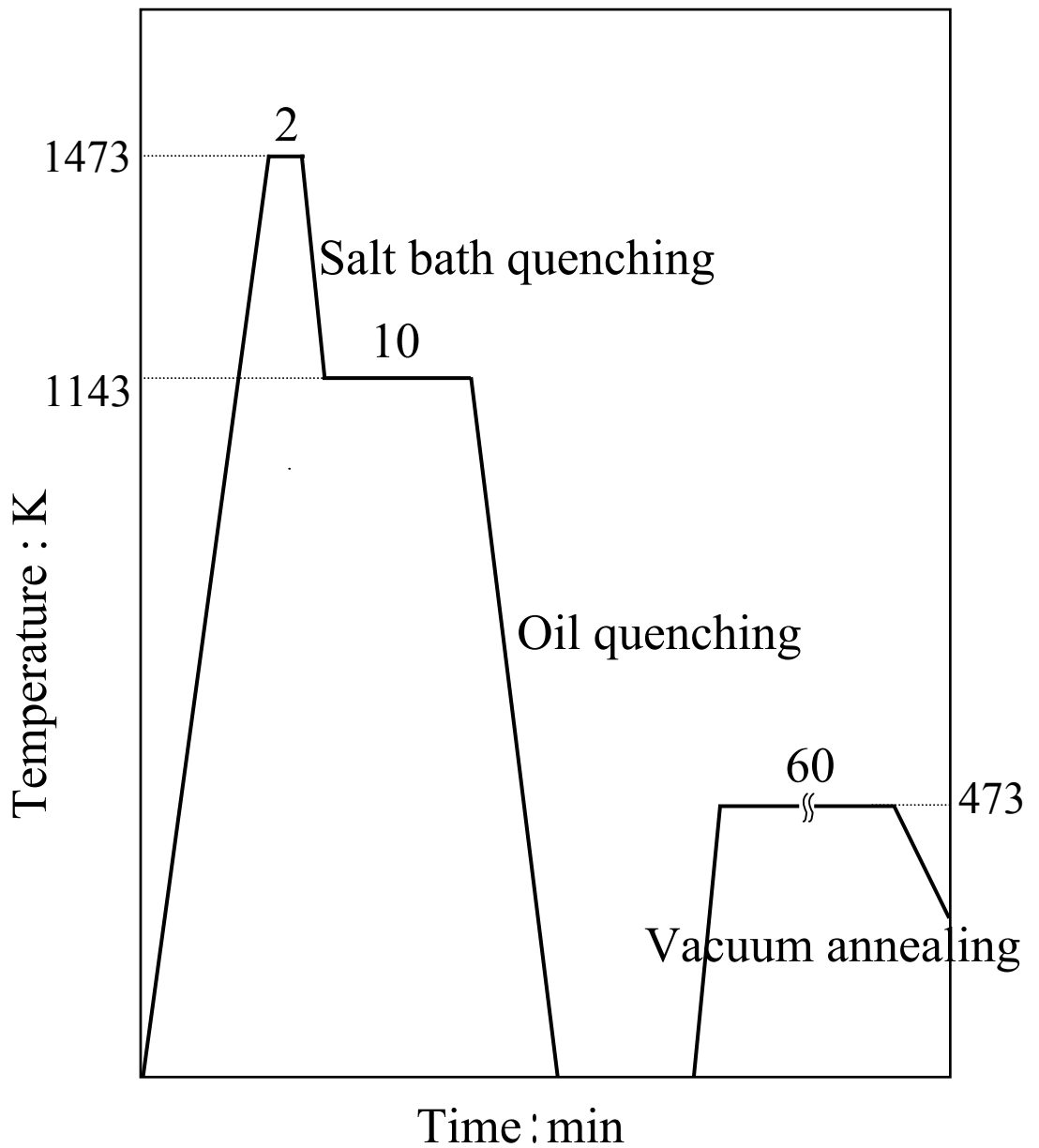


Fig. 2-5-(a). Schematic diagram showing heat treatment of ASTM A490 steel.

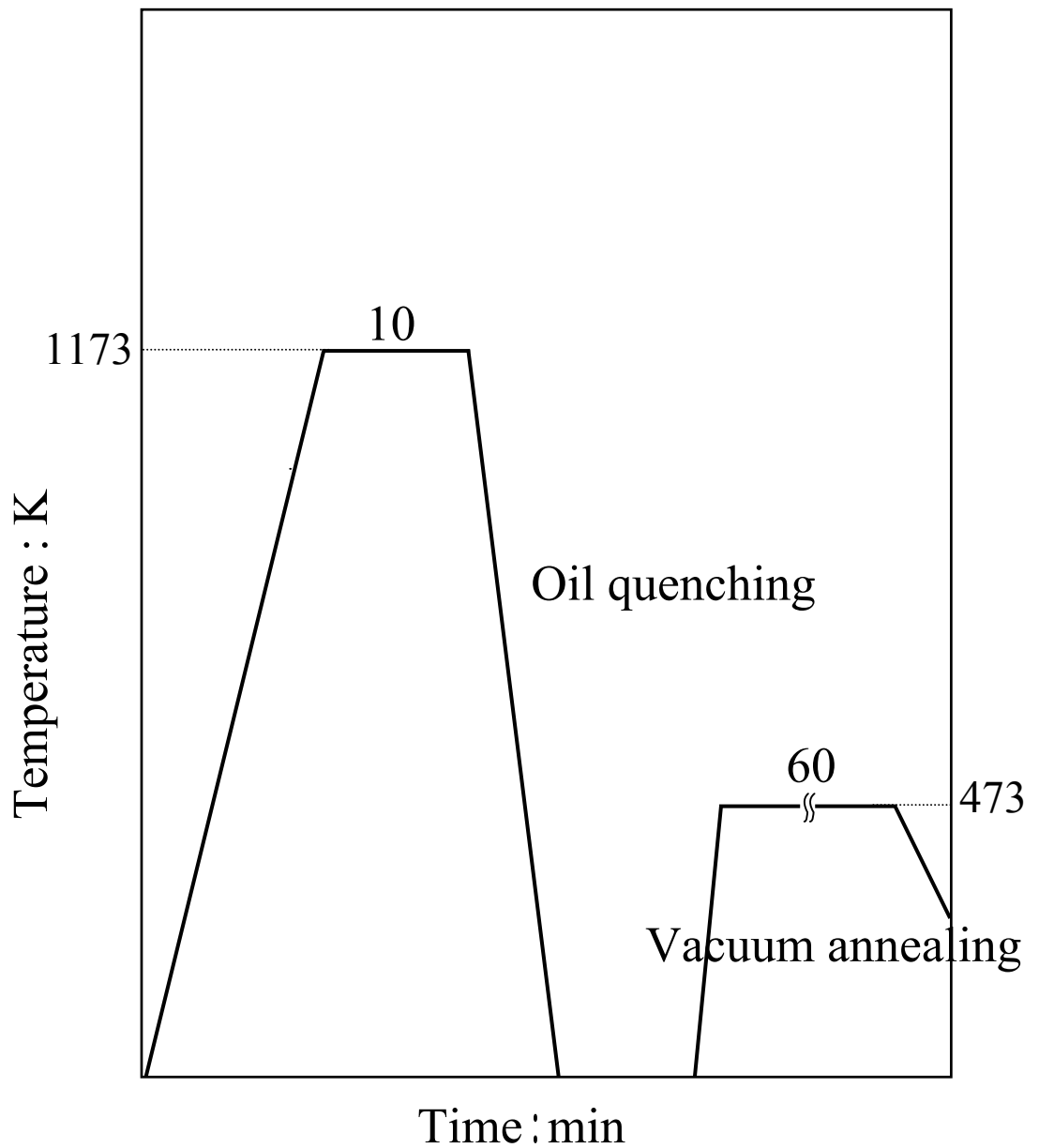


Fig. 2-5-(b). Schematic diagram showing heat treatment of S35C steel.

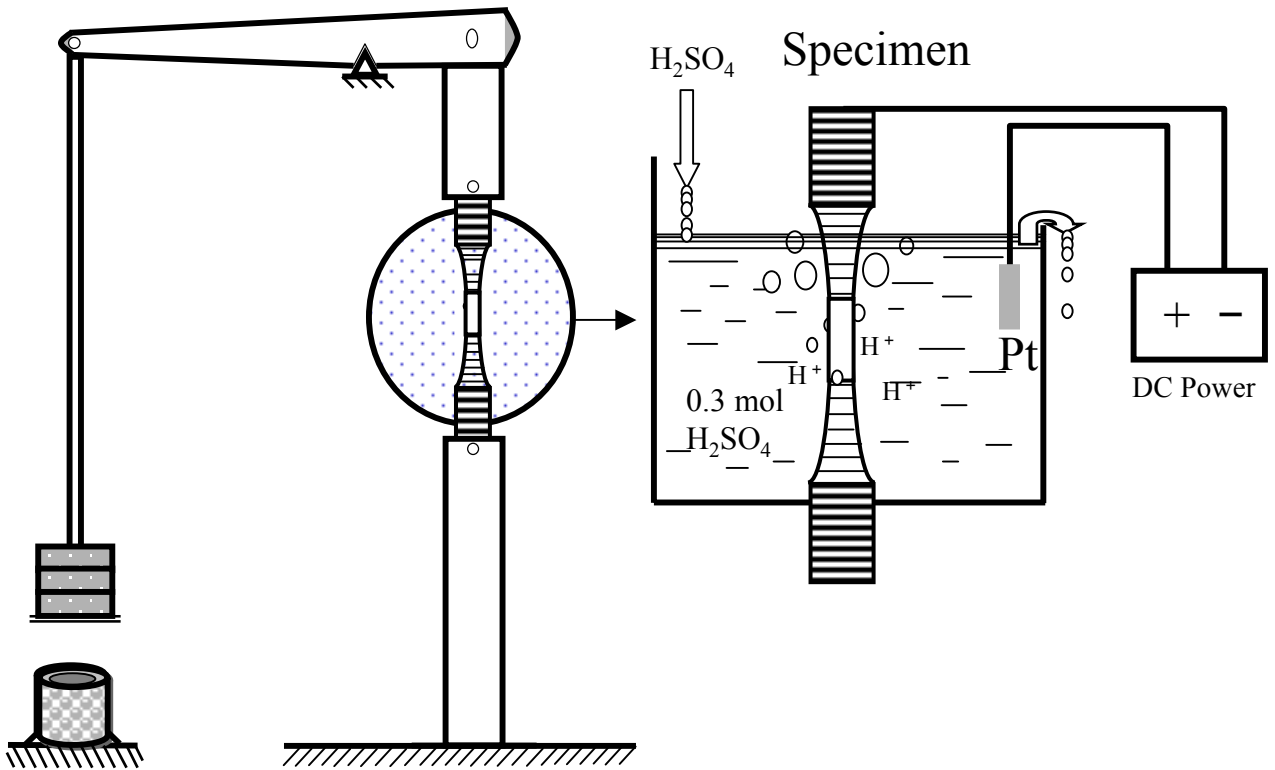


Fig. 2-6. Three-ton-creep test apparatus and hydrogen charge by cathode electrolysis method in sulfate solution.

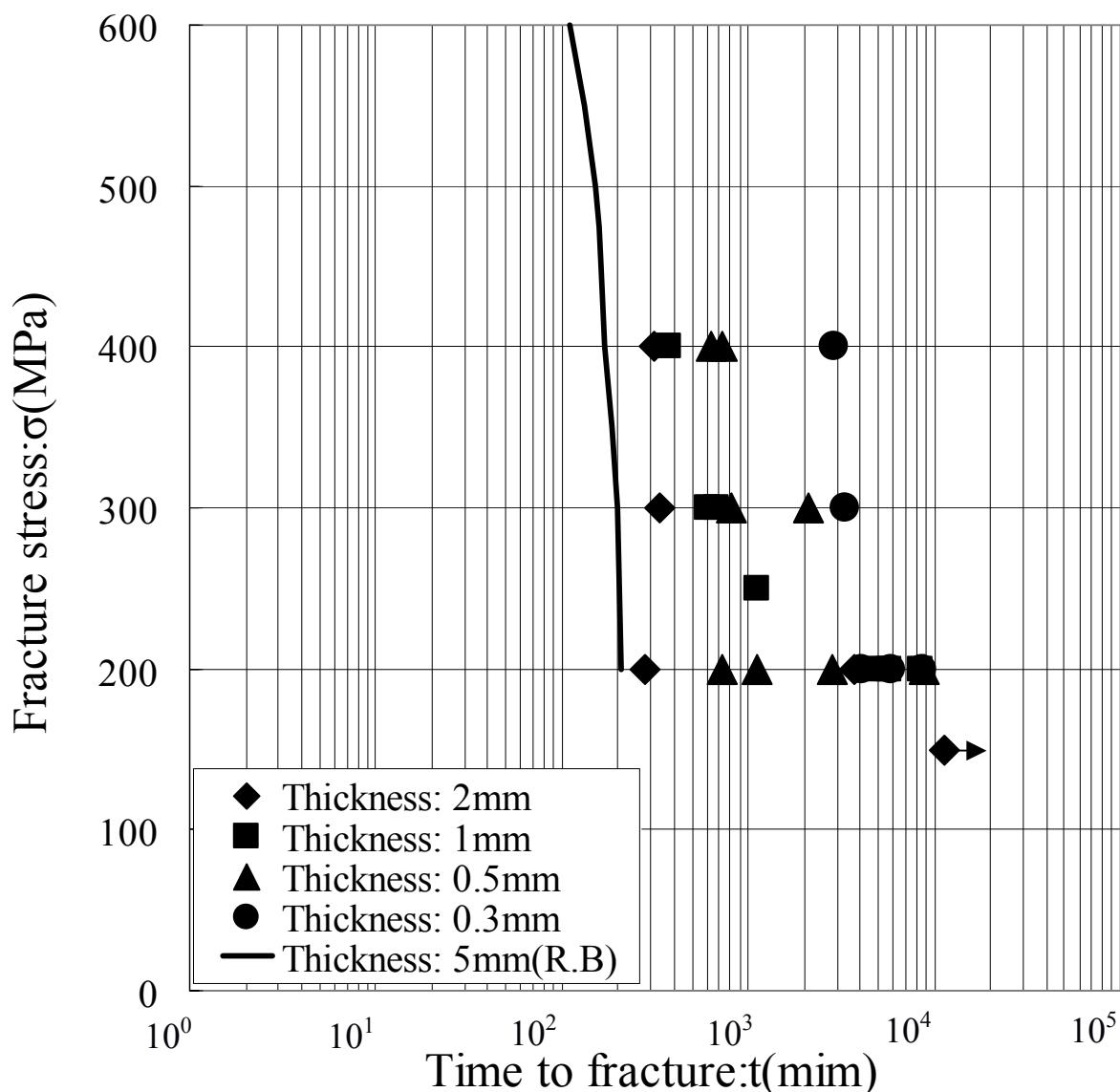


Fig. 2-7. Relationship between fracture stress and time to fracture in delayed fracture of ASTM A490 steel.

(The line in the figure indicates the results of the round bar specimen with the diameter of 5mm)

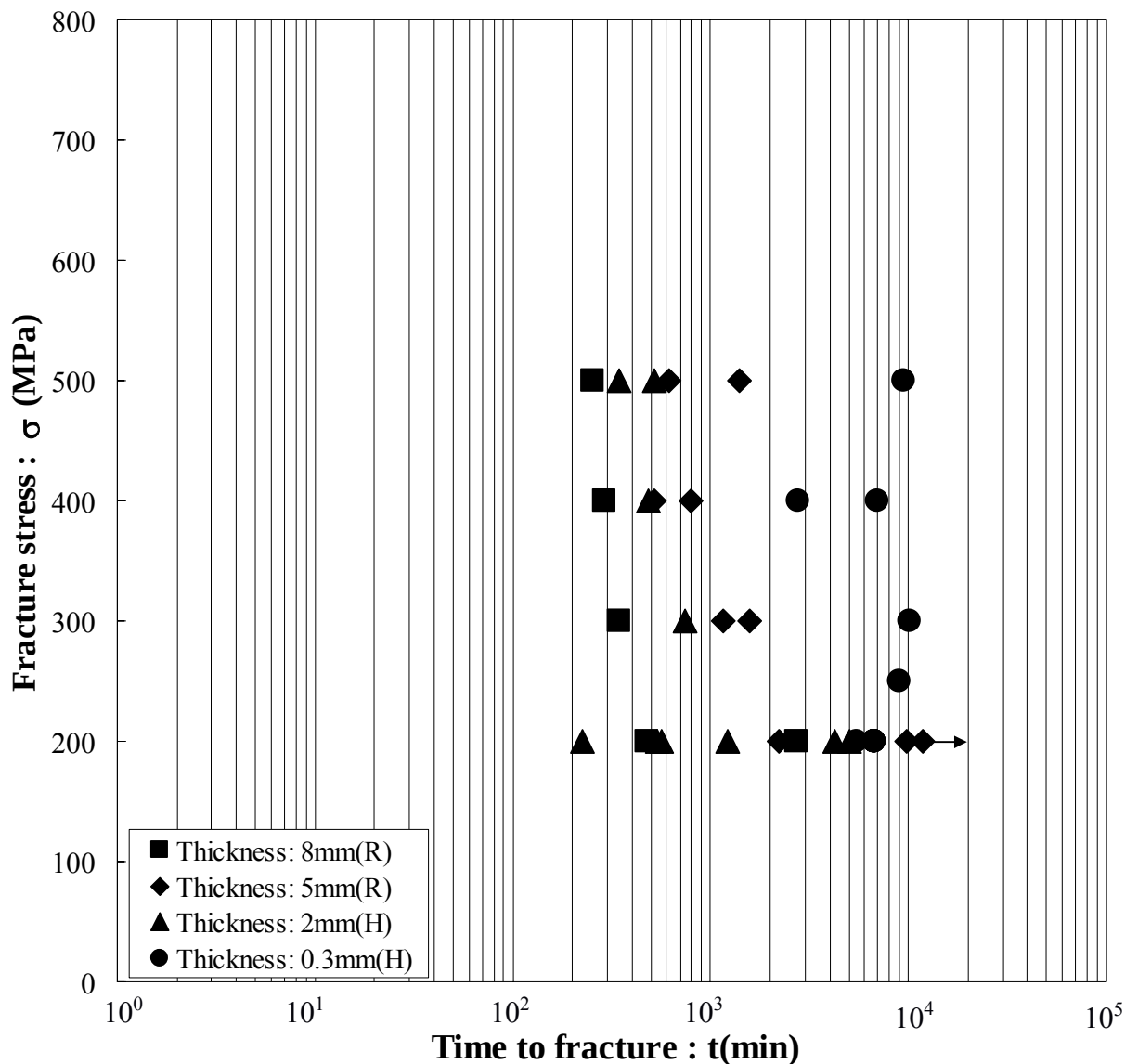
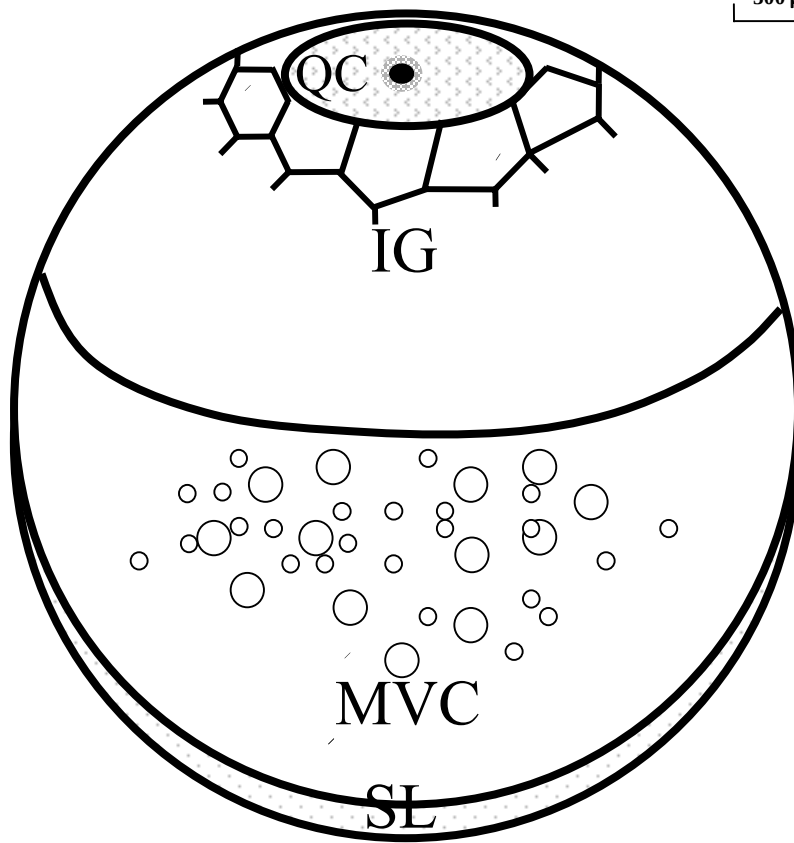
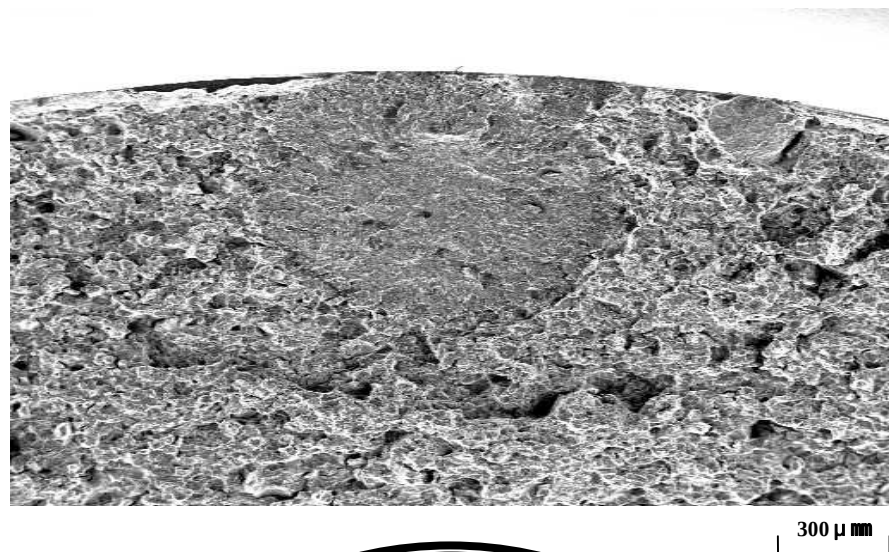
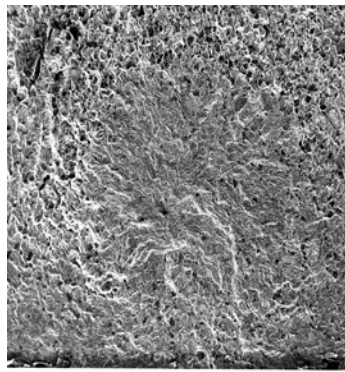


Fig. 2-8. Relationship between fracture stress and time to fracture in delayed fracture of Q/T S35C steel.

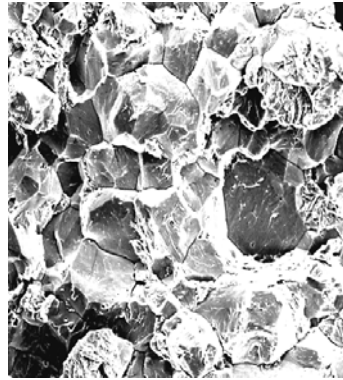


QC: Quasi-cleavage crack IG: Intergranular crack
 MVC: Micro-void coalescence SL: Shear lip

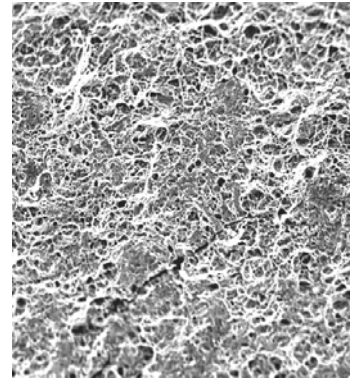
Fig. 2-9. SEM fractograph and schematic illustration of crack propagation mode in the fracture surface of solid specimen of Q/T S35C steel with 5mm and 8mm diameters.



QC facet



IG facet



MVC facet

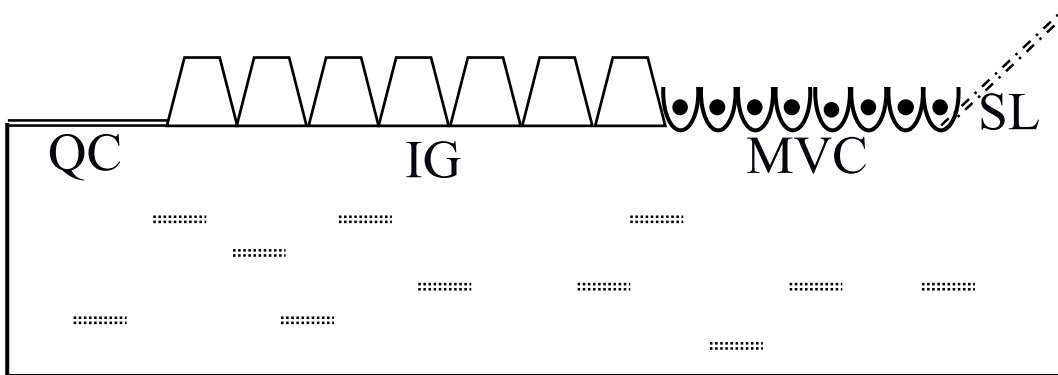
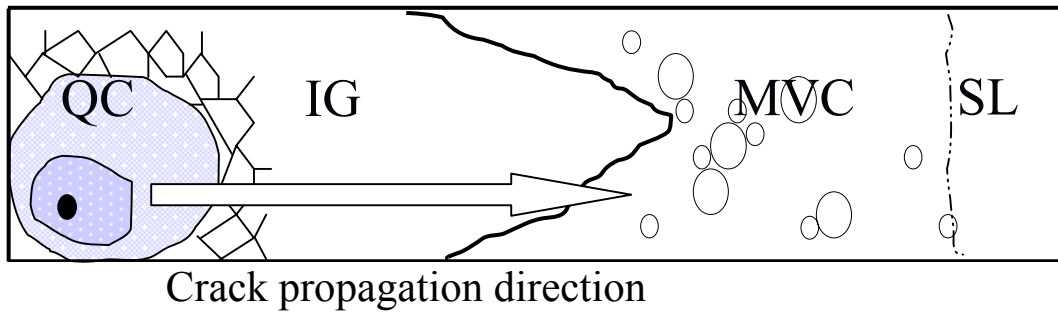
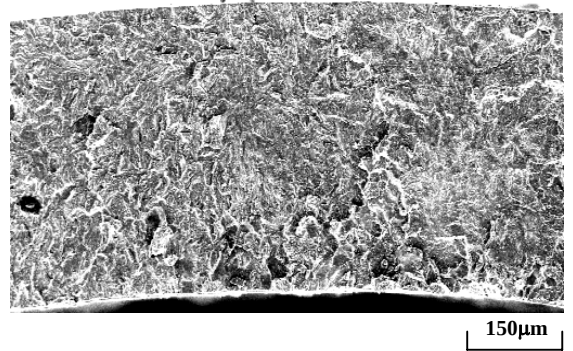
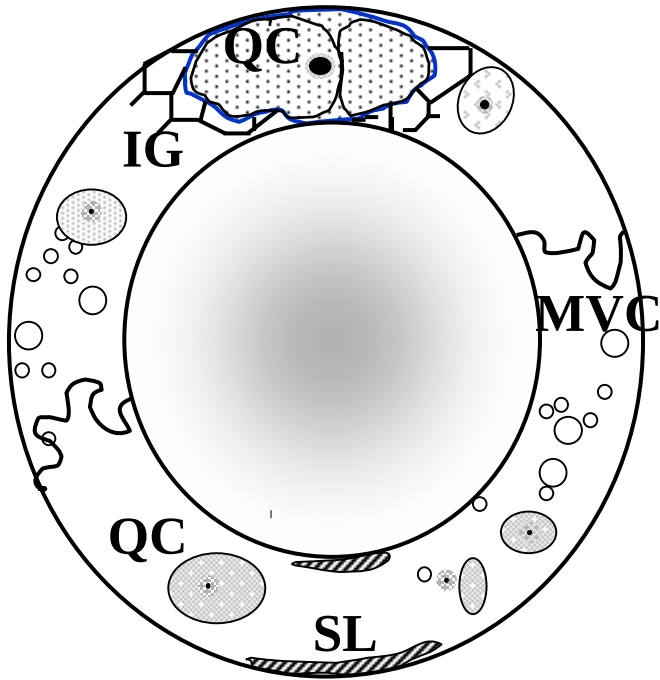
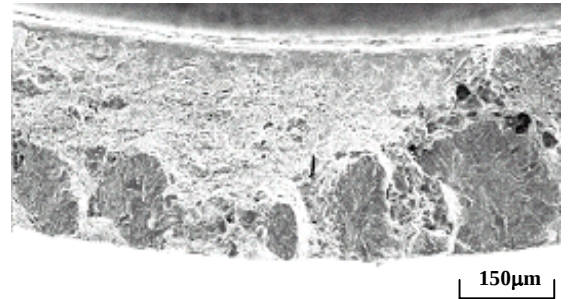


Fig. 2-10. SEM fractographs and fracture morphologies in thin plate specimens of ASTM A490 steel having thickness greater than 1mm.

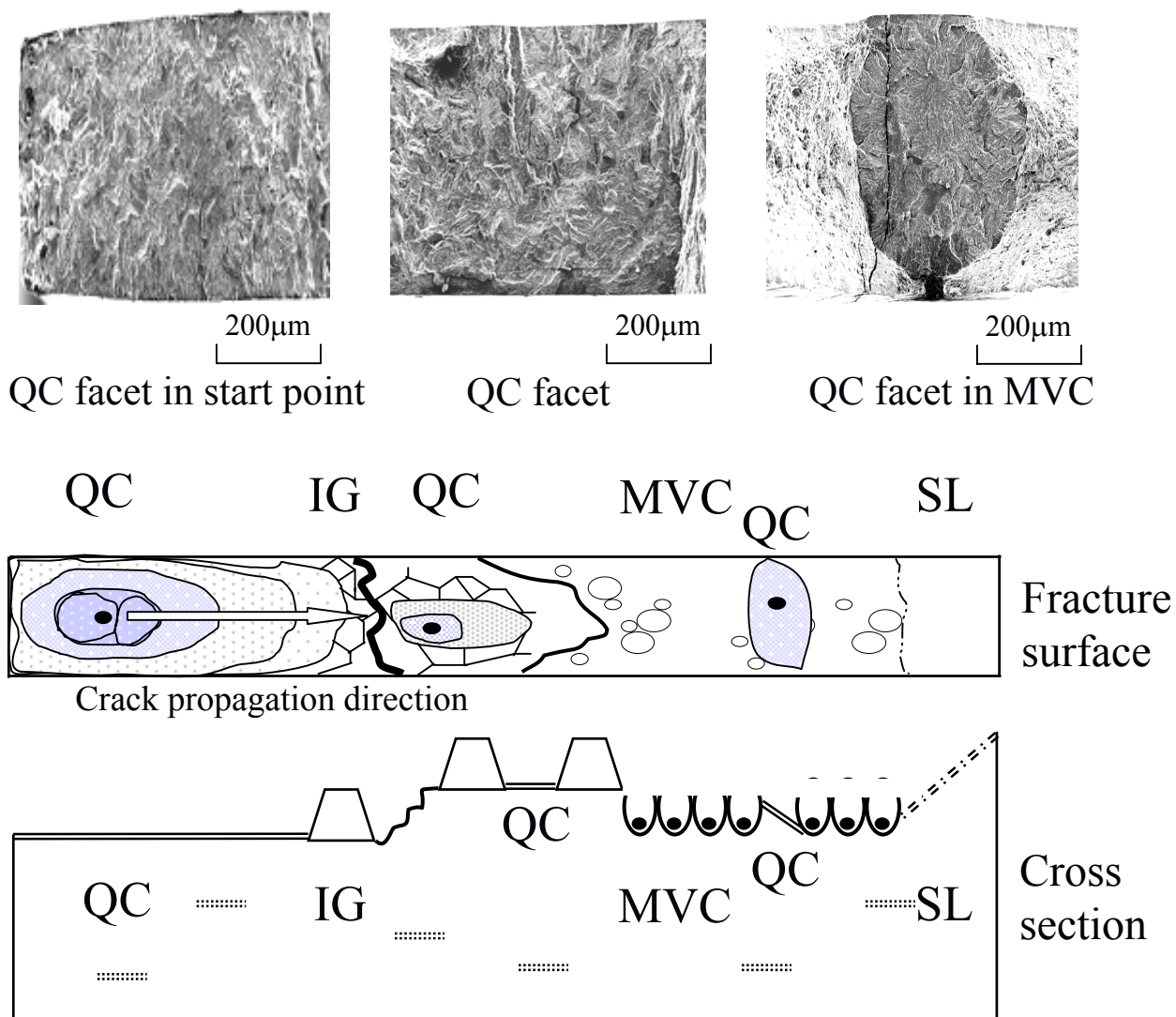


QC facets



QC facets in the MVC

Fig. 2-11. SEM fractographs and a schematic illustration of cracking process in a fracture surface of the thin walled hollow specimen of Q/T S35C steel with 0.3mm wall thickness.



Typical fracture facet having irregular morphology in thin plate specimen : $t < 0.5\text{mm}$

Fig. 2-12. SEM fractographs and fracture morphologies in thin plate specimen of ASTM A490 steel having thickness less than 0.5mm .

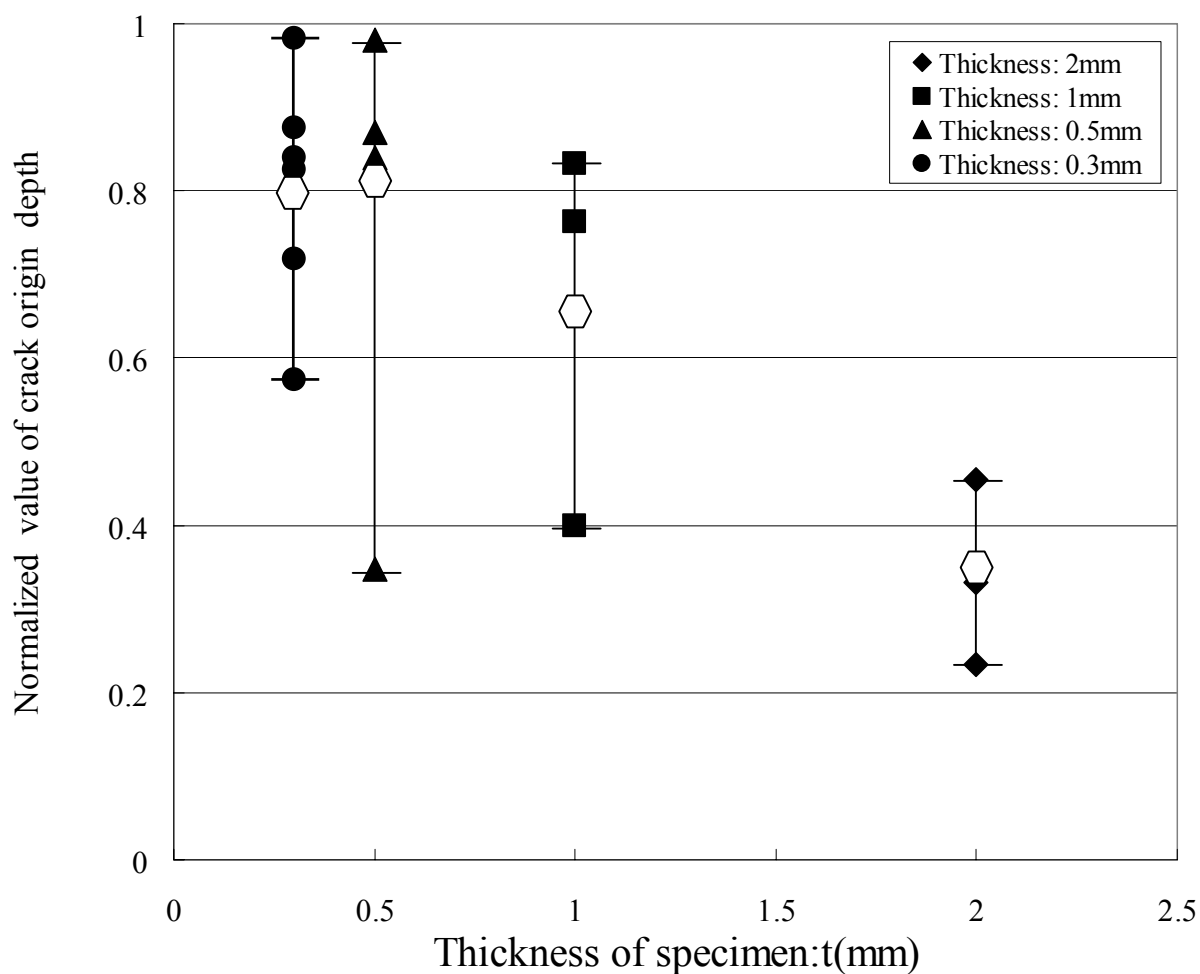


Fig. 2-13. Relationship between depth of crack origin from specimen surface and specimen thickness in ASTM A490 steel.

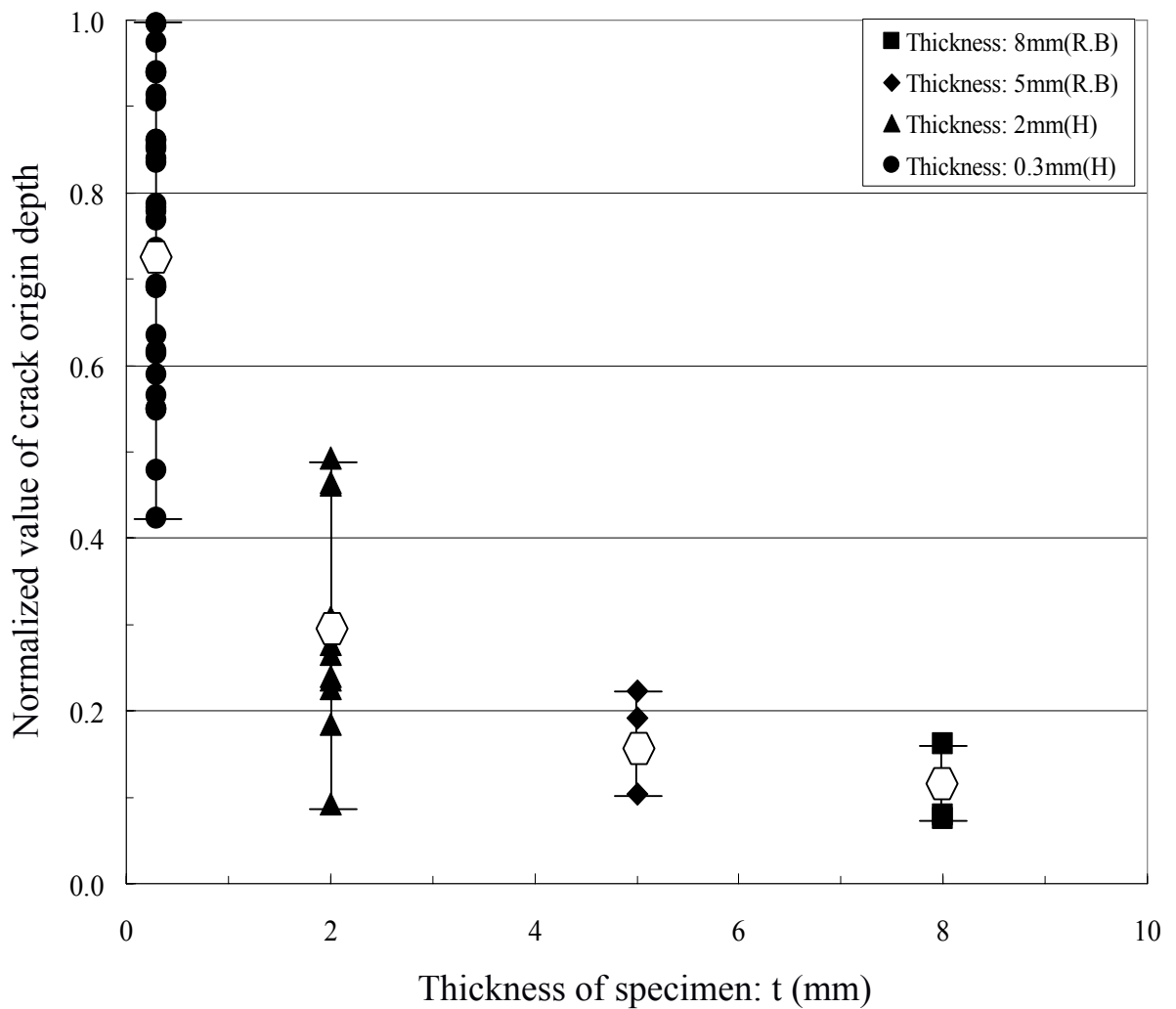
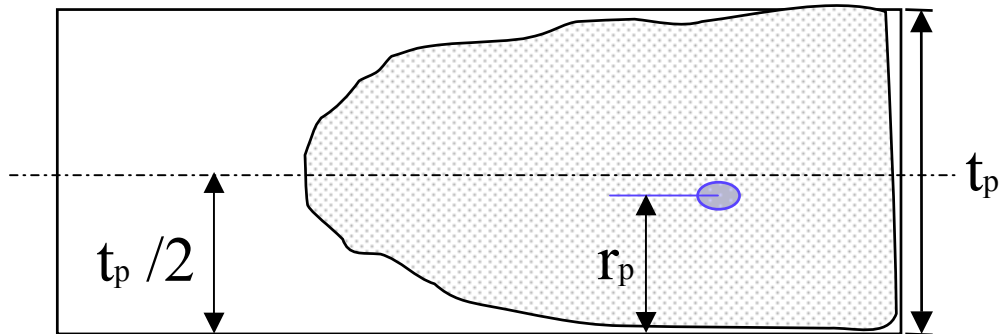
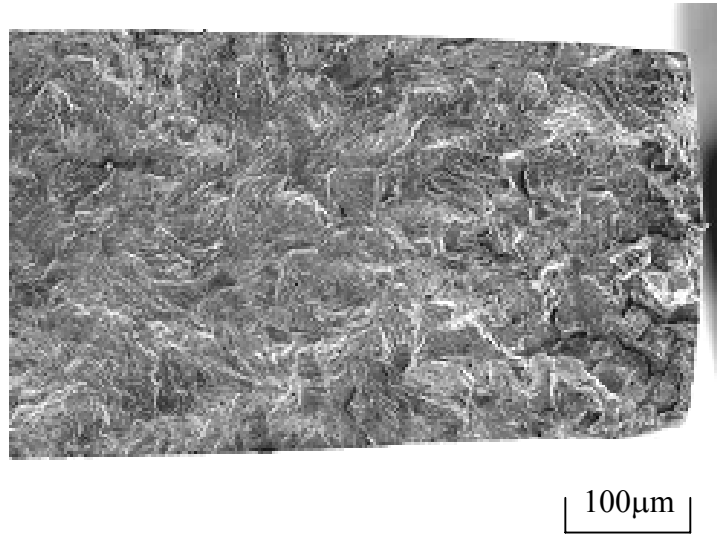
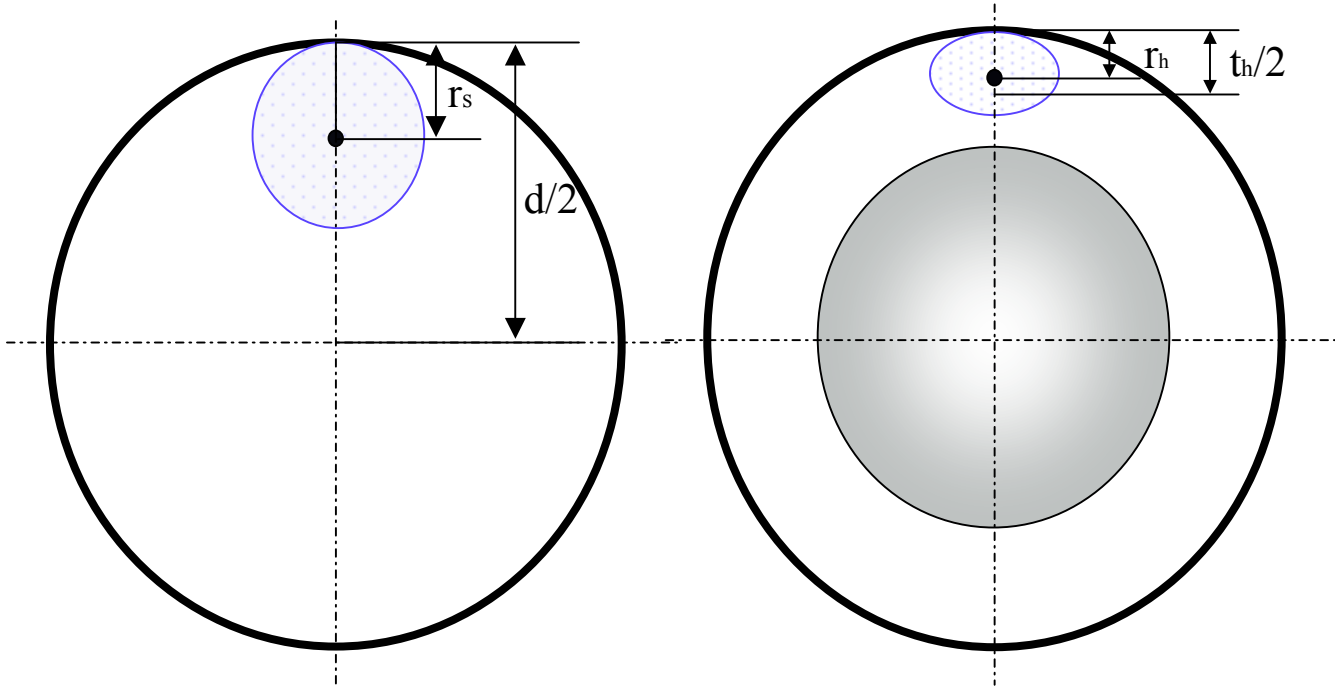


Fig. 2-14. Relationship between depth of crack origin from specimen surface and specimen thickness in Q/T S35C steel.



$$\text{N.C.O.D} = r_p / (t_p / 2) \quad \left\{ \begin{array}{l} 1: \text{Center} \\ 0: \text{Surface} \end{array} \right.$$

Fig. 2-15. SEM fractograph and and depth of crack origin from the side wall of specimen surface in thin plate specimens of ASTM A490 steel (0.3mm t 2mm).



$$\text{N.C.O.D} = r_s / (d/2) \text{ or } r_h / (t_h/2)$$

$\left\{ \begin{array}{l} 1: \text{Center} \\ 0: \text{Surface} \end{array} \right.$

Fig. 2-16. Depth of crack origin from specimen surface in a solid and thin walled hollow specimen of Q/T S35C steel ($d=5,8\text{mm}$, $t=0.3,2\text{mm}$).

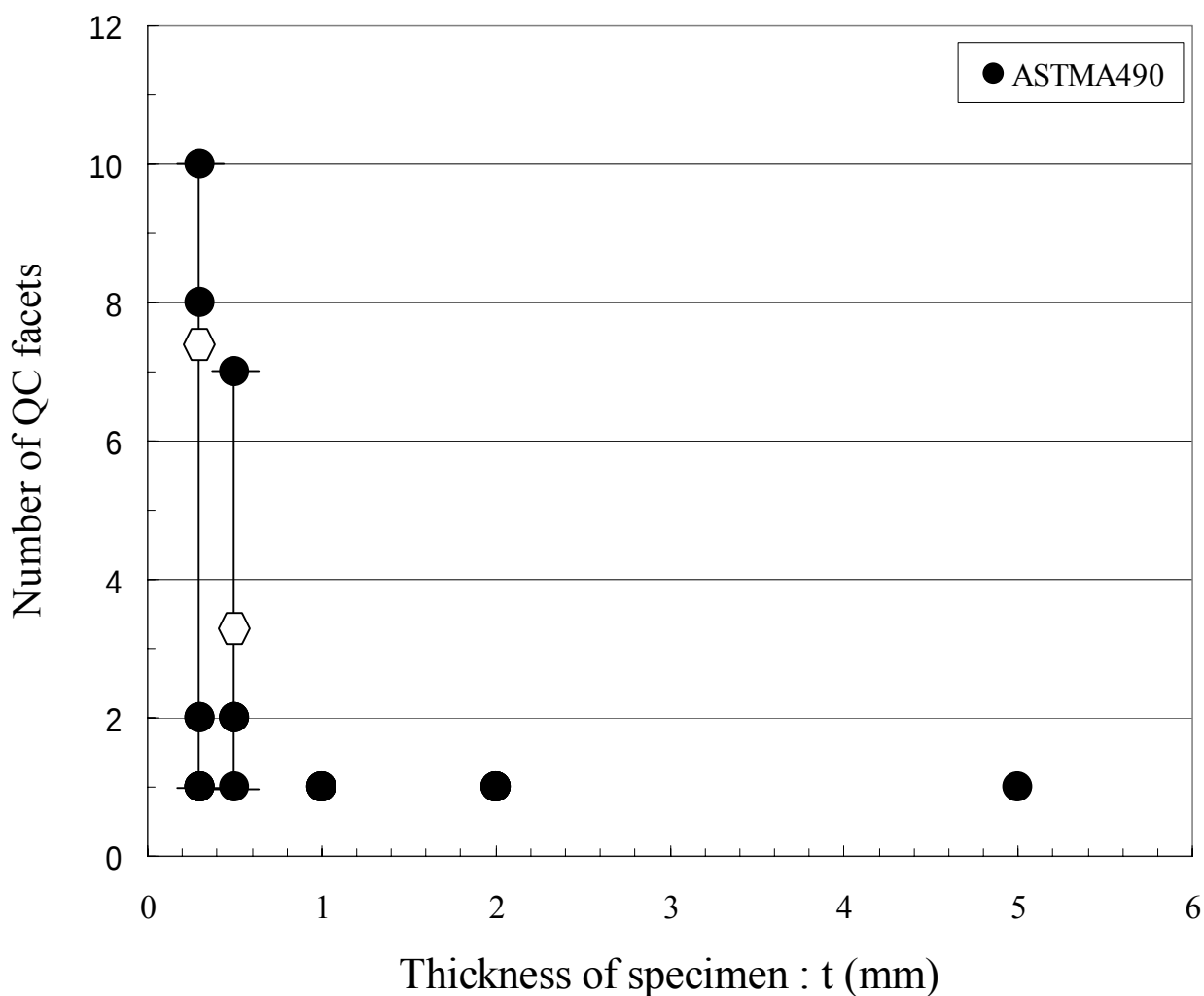


Fig. 2-17. Relationship between number of QC facets and specimen thickness for ASTM A490 steel.

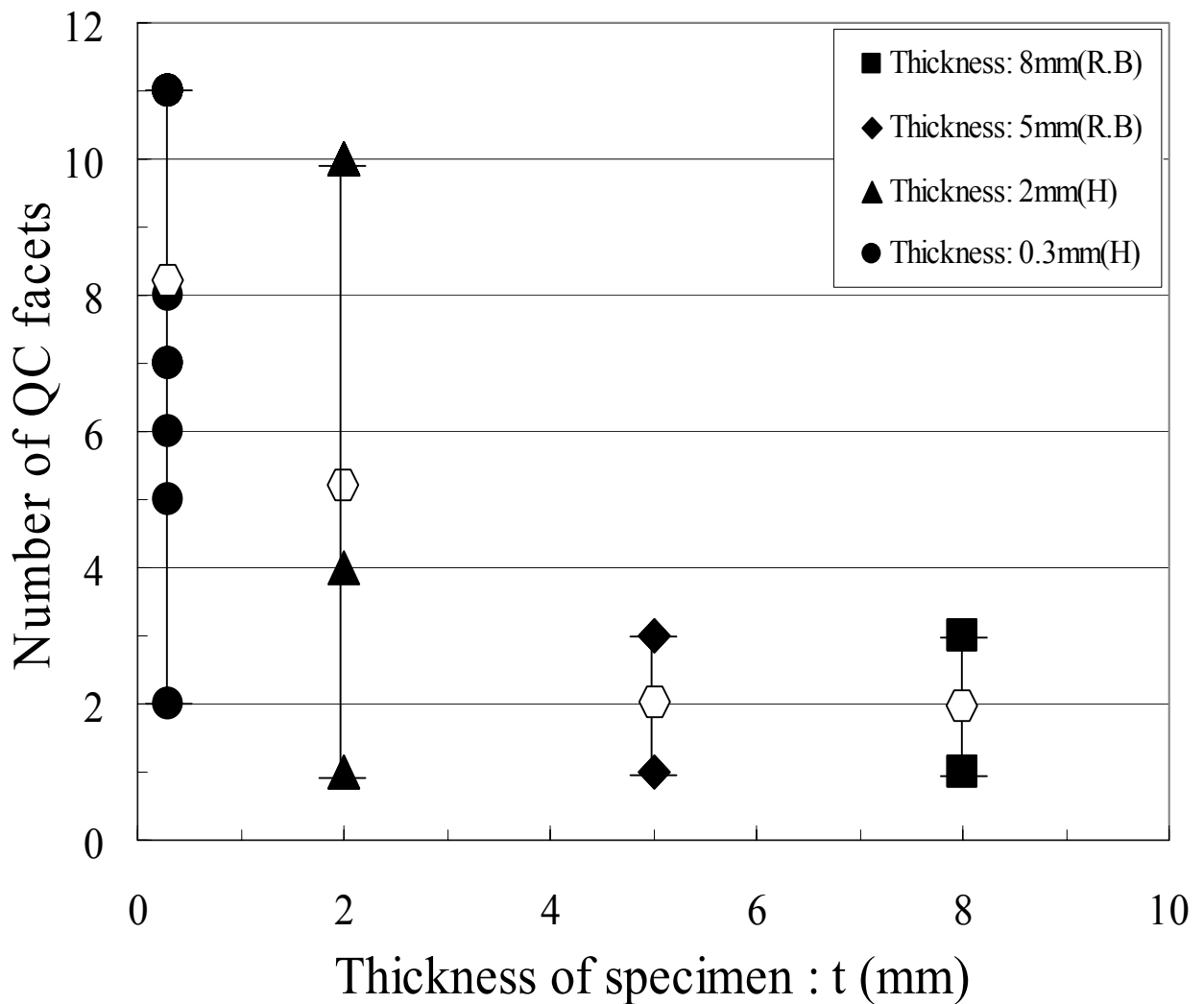
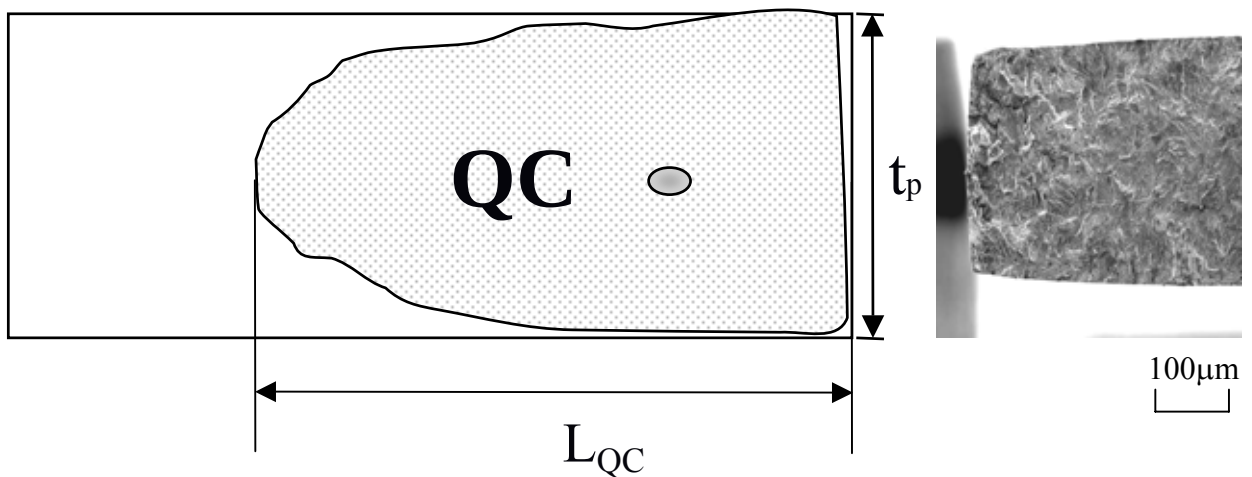
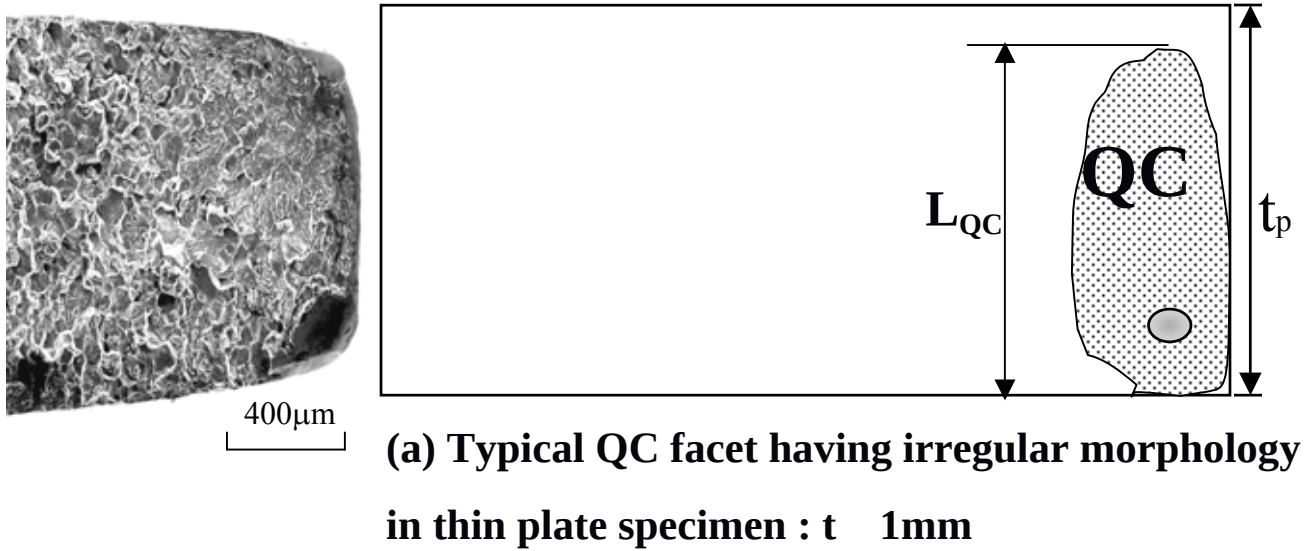
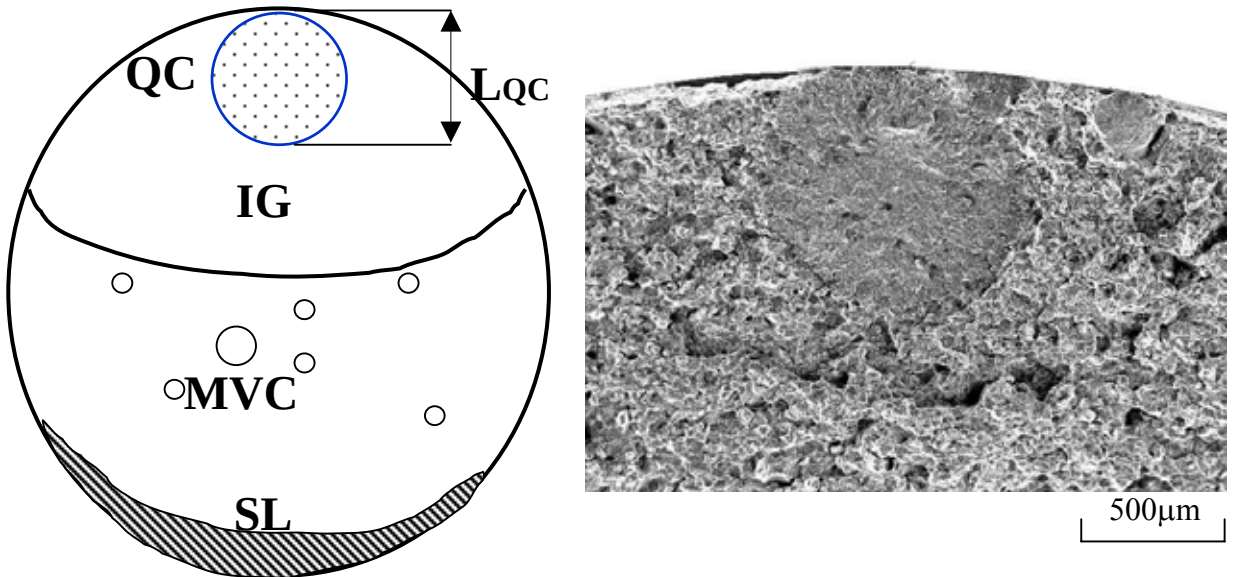


Fig. 2-18. Relationship between number of QC facets and specimen thickness for Q/T S35C steel.

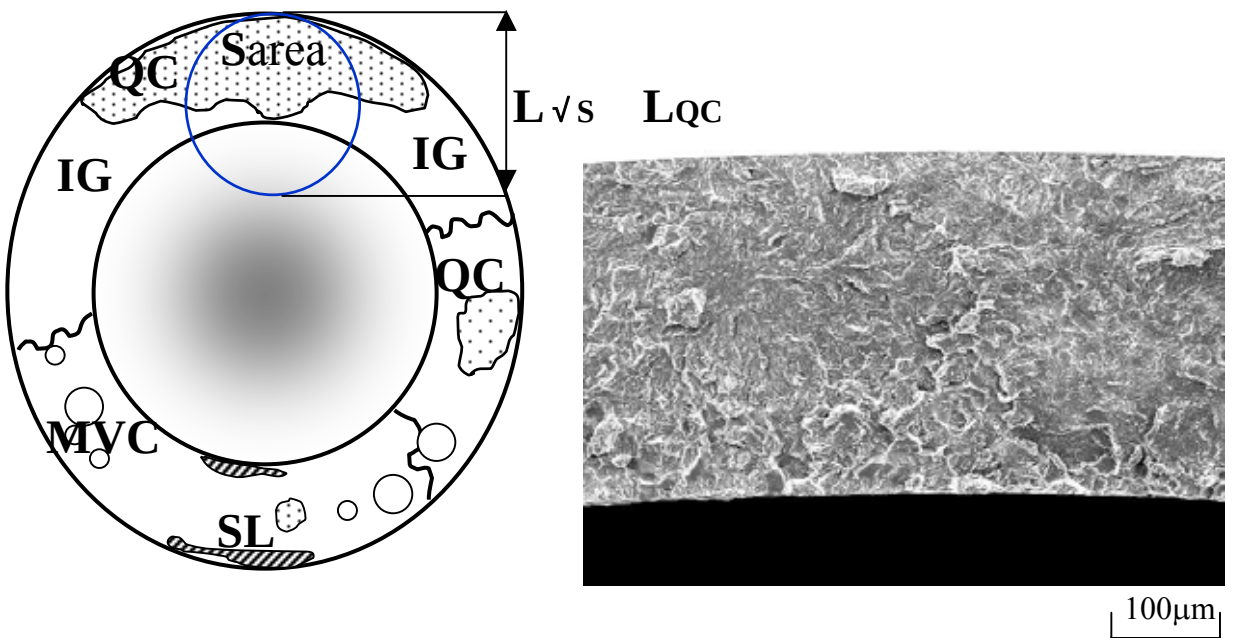


(b) Typical QC facet having irregular morphology in thin plate specimen : $t = 0.5\text{mm}$

Fig. 2-19. SEM fractographs and critical crack length (L_{QC}) measured as the maximum length along the direction of thickness and width in a plate specimen of ASTM A490 steel ($0.3\text{mm} \leq t \leq 2\text{mm}$).



(a) Typical morphology of QC facet in the round bar and hollow specimens (d=5mm, 8mm)



(b) Typical QC facet having unusual morphology in thin hollow specimen (t=0.3mm)

Fig. 2-20. SEM fractographs and evaluation of the critical crack length in a thin walled hollow specimen of Q/T S35C using the root area method[105-106].

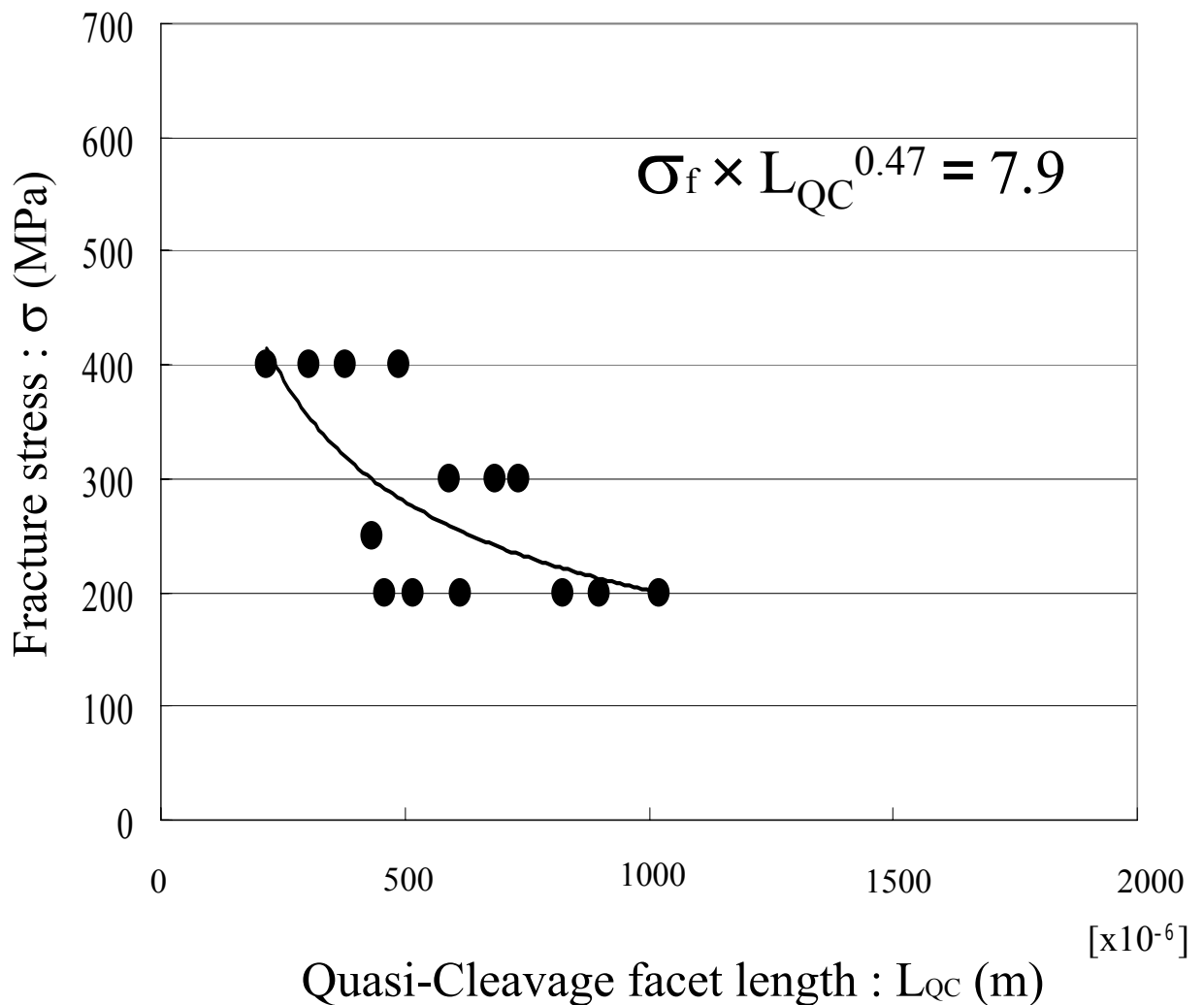


Fig. 2-21. Relationship between fracture stress and QC facet length in thin plate specimens of ASTM A490 steel.

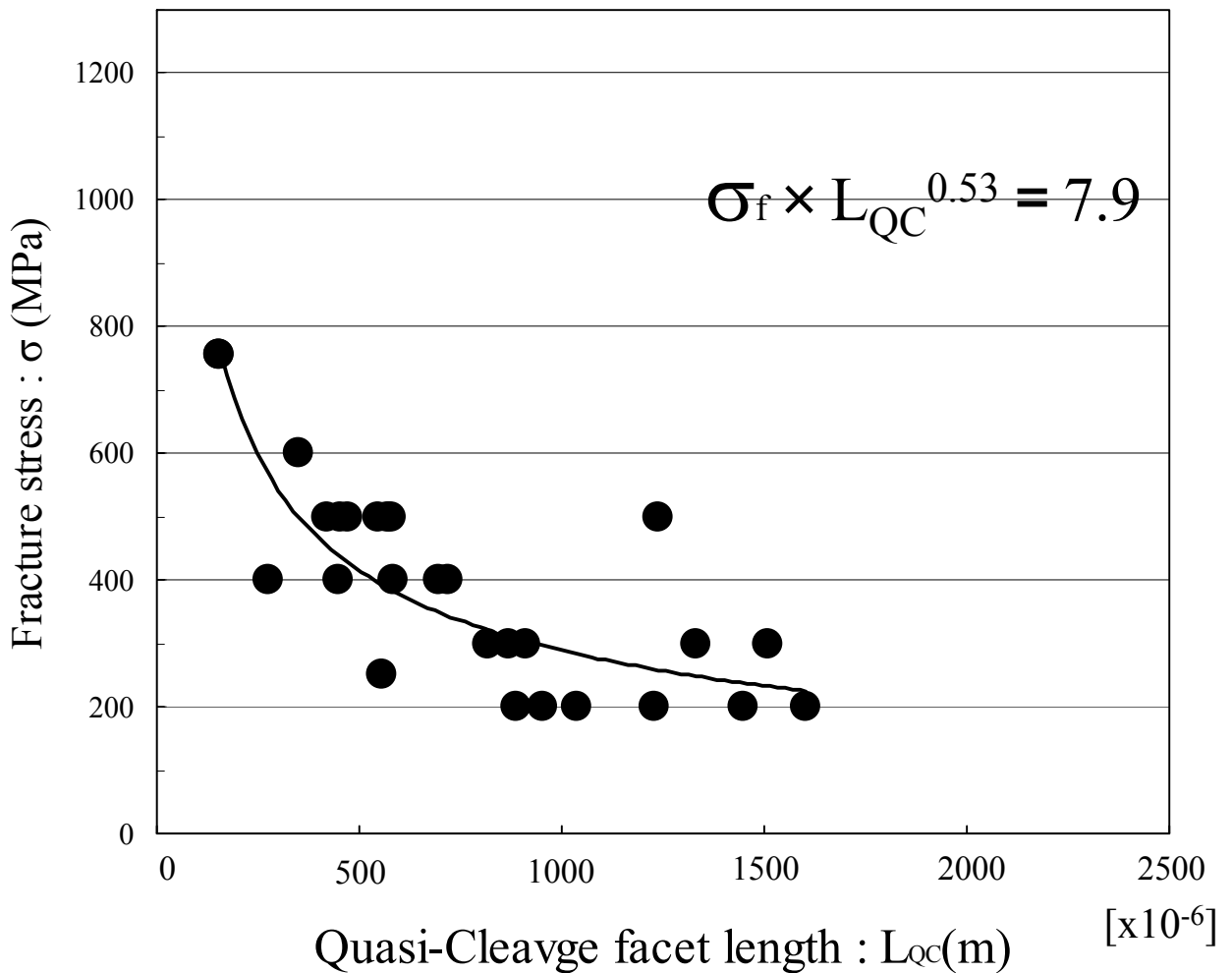


Fig. 2-22. A classical Griffith relationship between fracture stress and QC facet length in solid and hollow specimens of Q/T S35C steel.

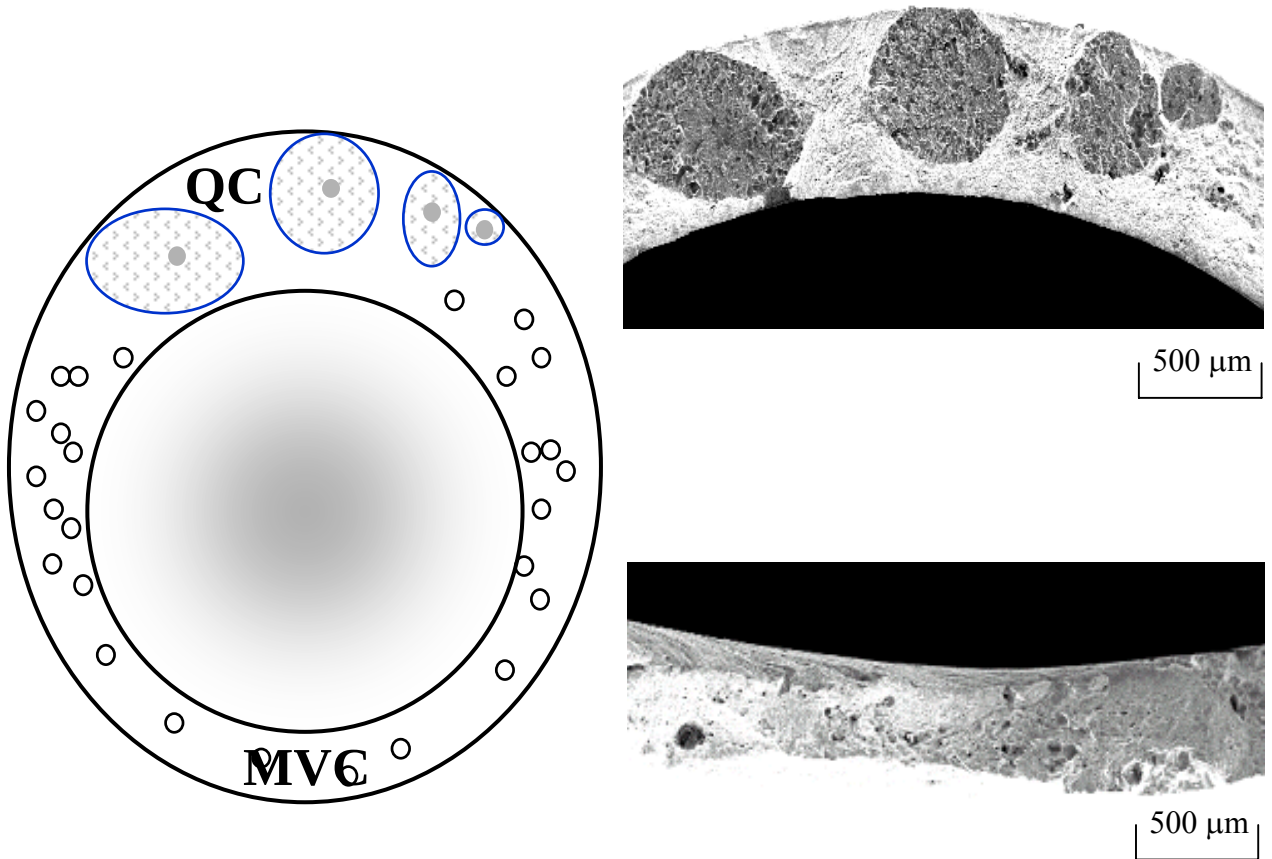


Fig. 2-23. SEM fractographs and schematic illustration of cracking process in the fracture surface of an eccentrically bored hollow specimen of Q/T S35C steel.

Table 3-1. Chemical compositions of specimens

wt%

Materials	C	Si	Mn	P	S	Cr	Mo	Ni	Fe
ASTM A490	0.33	0.16	0.68	0.016	0.01	0.79	0.16	—	Bal
S35C (AISI 1035)	0.36	0.24	0.75	0.1	0.15	0.11	—	—	Bal
API X65	0.07	0.24	1.48	0.008	0.0013	0.035	—	0.027	Bal

Table 3-2. Mechanical Properties of specimens

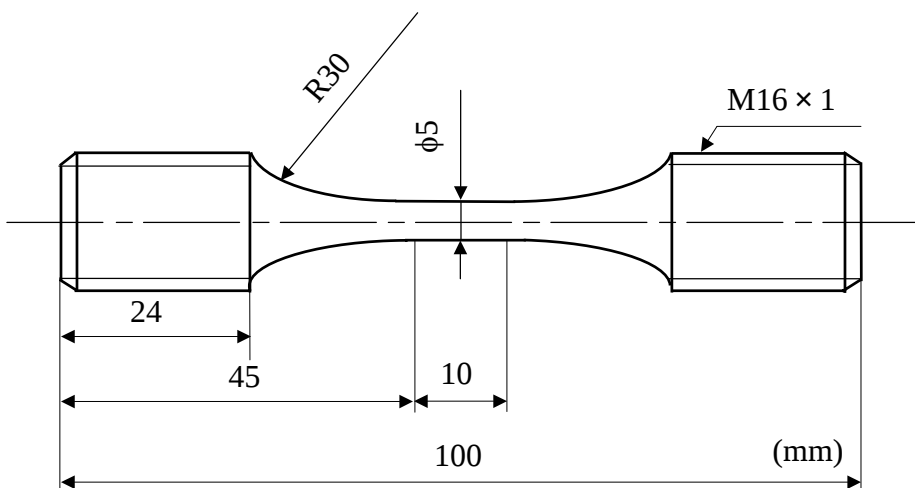
<i>Materials</i>	<i>Tempering Temperature (K)</i>	<i>U.T.S (MPa)</i>	<i>0.2% Proof stress (MPa)</i>	<i>Micro-Vickers hardness (P=300g, 50points)</i>	<i>Threshold stress (MPa)</i>	<i>Elapsed loading time (min)</i>
API X65	473	880	709	360	500	10 ⁴
	*473	852	640	322	620	10 ⁴
	673	790	693	241	650	10 ⁴
	873	678	622	206	600	10 ⁴
ASTM A490	473	1734	1344	554	90	10 ⁴
	523	1630	1390	525	120	10 ⁴
	573	1577	1409	510	130	10 ⁴
	623	1475	1339	483	130	10 ⁴
	673	1352	1113	447	190	10 ⁴
	723	1214	1098	355	500	3x10 ³
	773	1119	989	338	750	3x10 ³
	873	936	816	284	750	3x10 ³
	973	767	674	245	620	3x10 ³
S35C (AISI 1035)	473	1360	1330	479	200	10 ⁴
	573	1369	1168	318	350	10 ⁴
	673	1128	976	329	500	10 ⁴
	723	876	822	268	650	10 ⁴
	773	785	690	264	600	10 ⁴
	973	632	523	180	475	10 ⁴

* 473K: Austenitized temperature of this particular specimen was at 1373K.

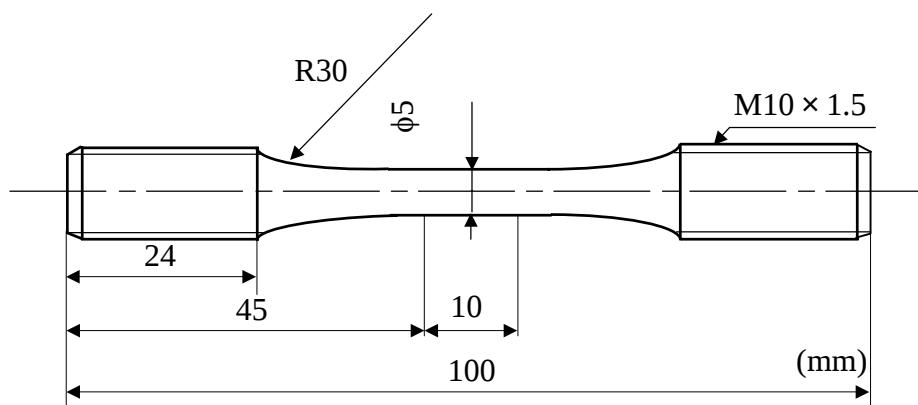
Table 3-3. Factors which affect the Crack propagation of delayed fracture in steels

Yield Strength level	Materials	Crack propagation model	Ratio of σ_{th}/σ_y
High strength steel	ASTM A490 (473K-623K) S35C(473K)	QC—IG—MVC	0.06-0.1
Medium strength steel	ASTM A490 (723K) S35C (673K)	QC—QC + IG—MVC	0.45-0.5
Low strength steel	ASTM A490 (773K-973K) S35C(723K-973K) APIX65(473K-873K)	QC—MVC	0.7-0.95
A general feature of crack propagation in steels		QC—IG, QC+IG - MVC	

* Numbers in parenthesis indicate the tempering temperature.



The specimens of ASTM A490 and S35C steels



The specimen of API X65 steel

Fig. 3-1. Shape and dimensions of unnotched specimens of ASTM A490, S35C and API X65 steels.

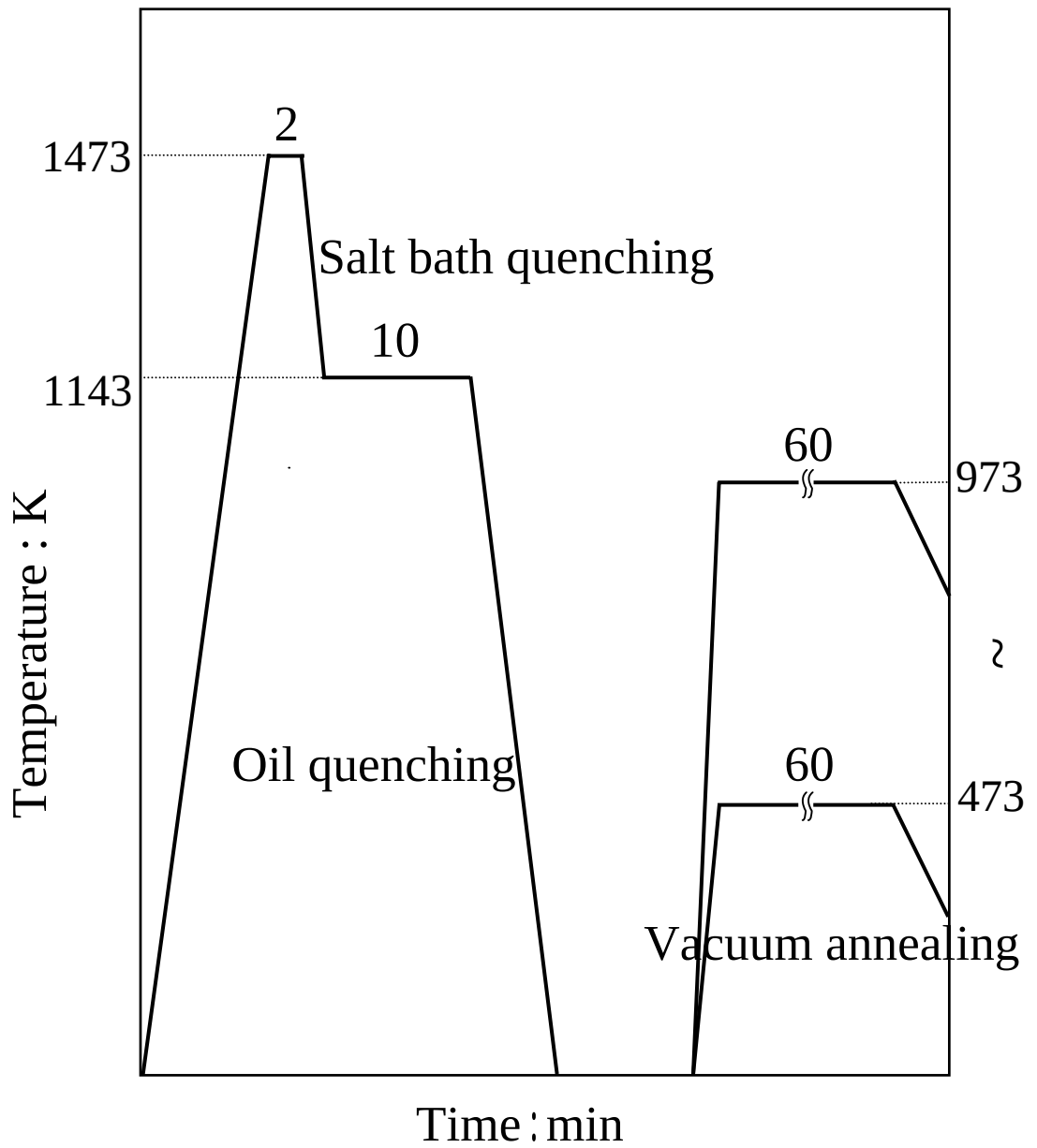


Fig. 3-2. Schematic illustration showing heat treatment of ASTM A490 steel.

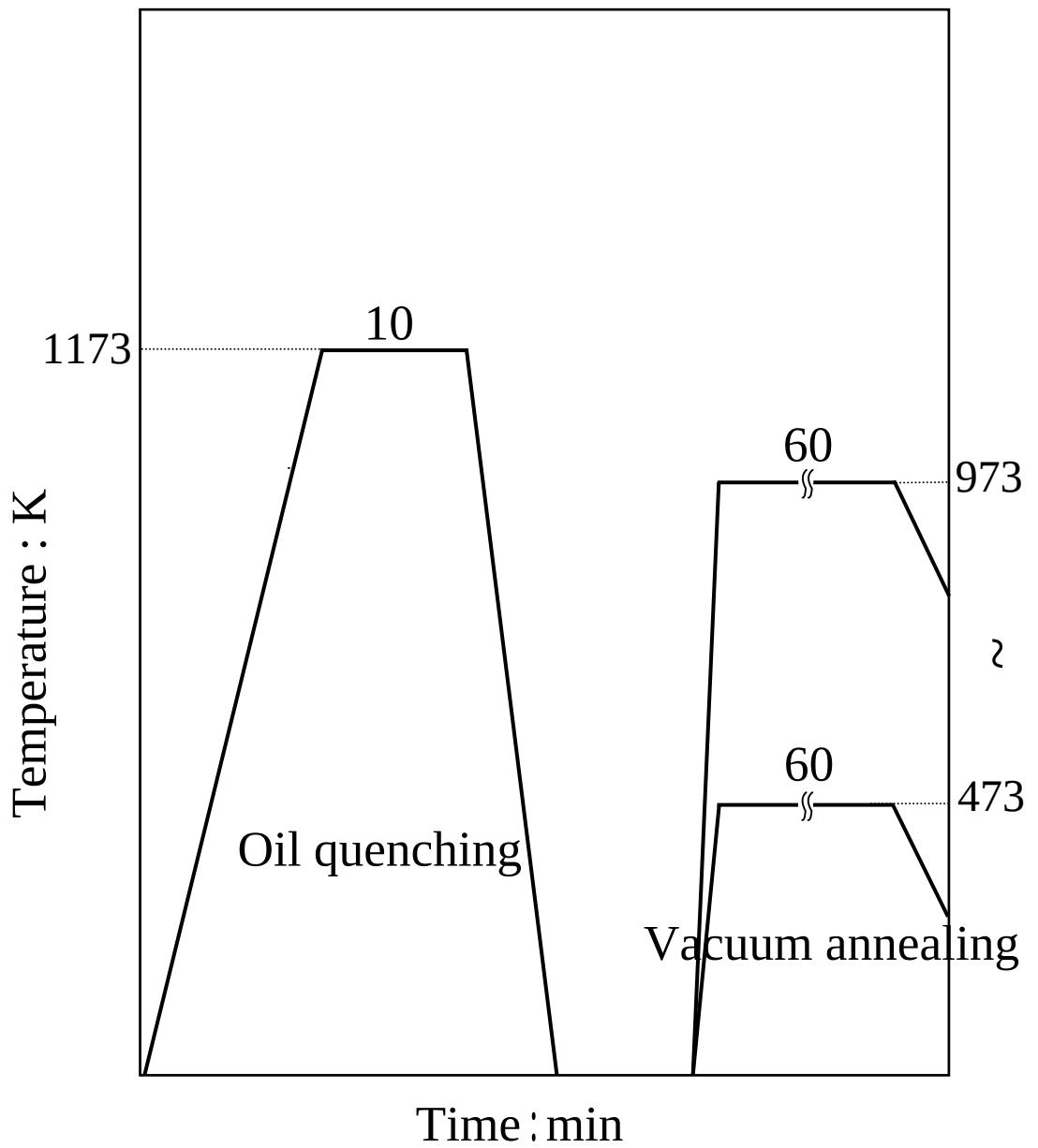


Fig. 3-3. Schematic illustration showing heat treatment of S35C steel.

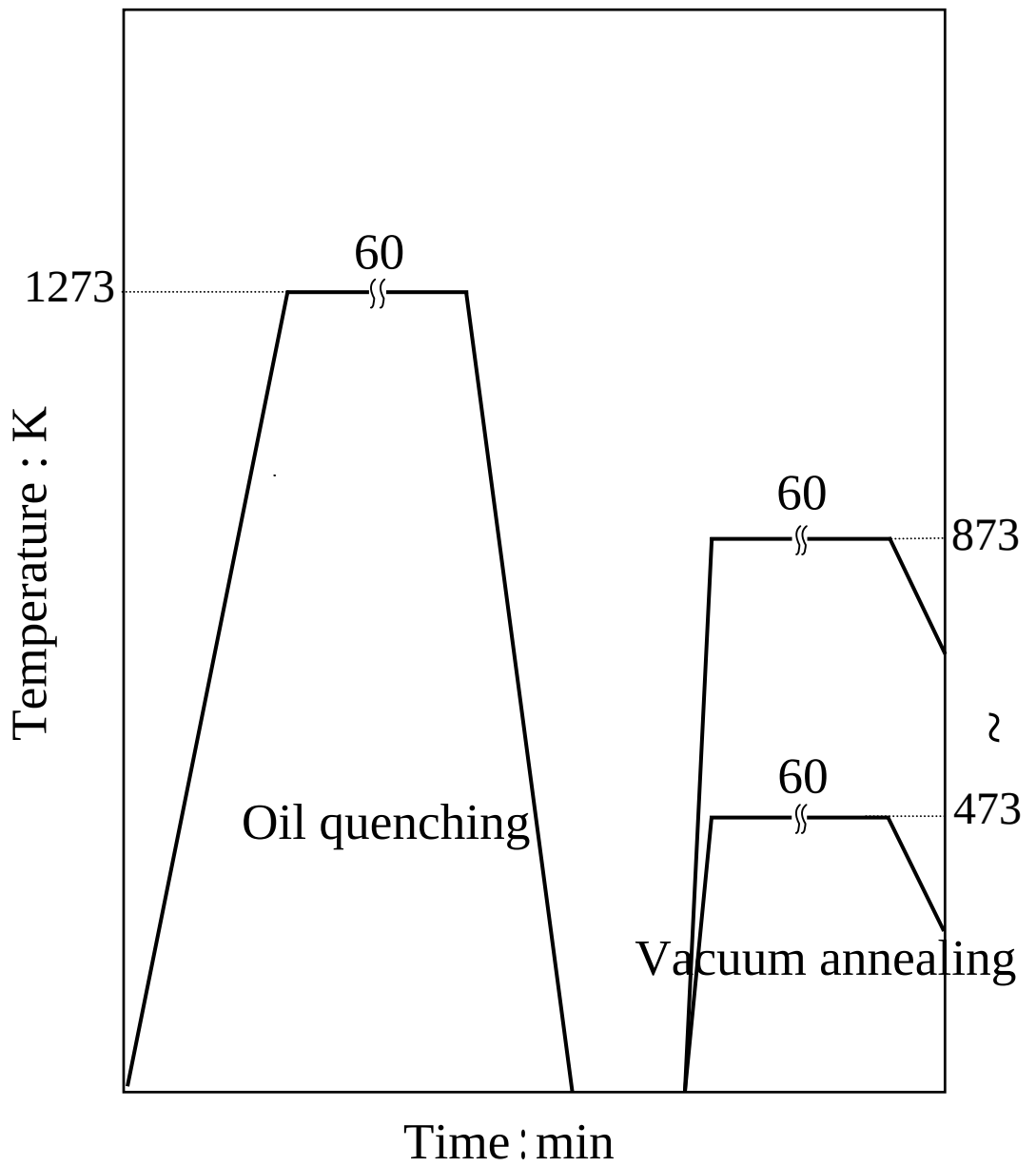


Fig. 3-4. Schematic illustration showing heat treatment of API X65 steel.

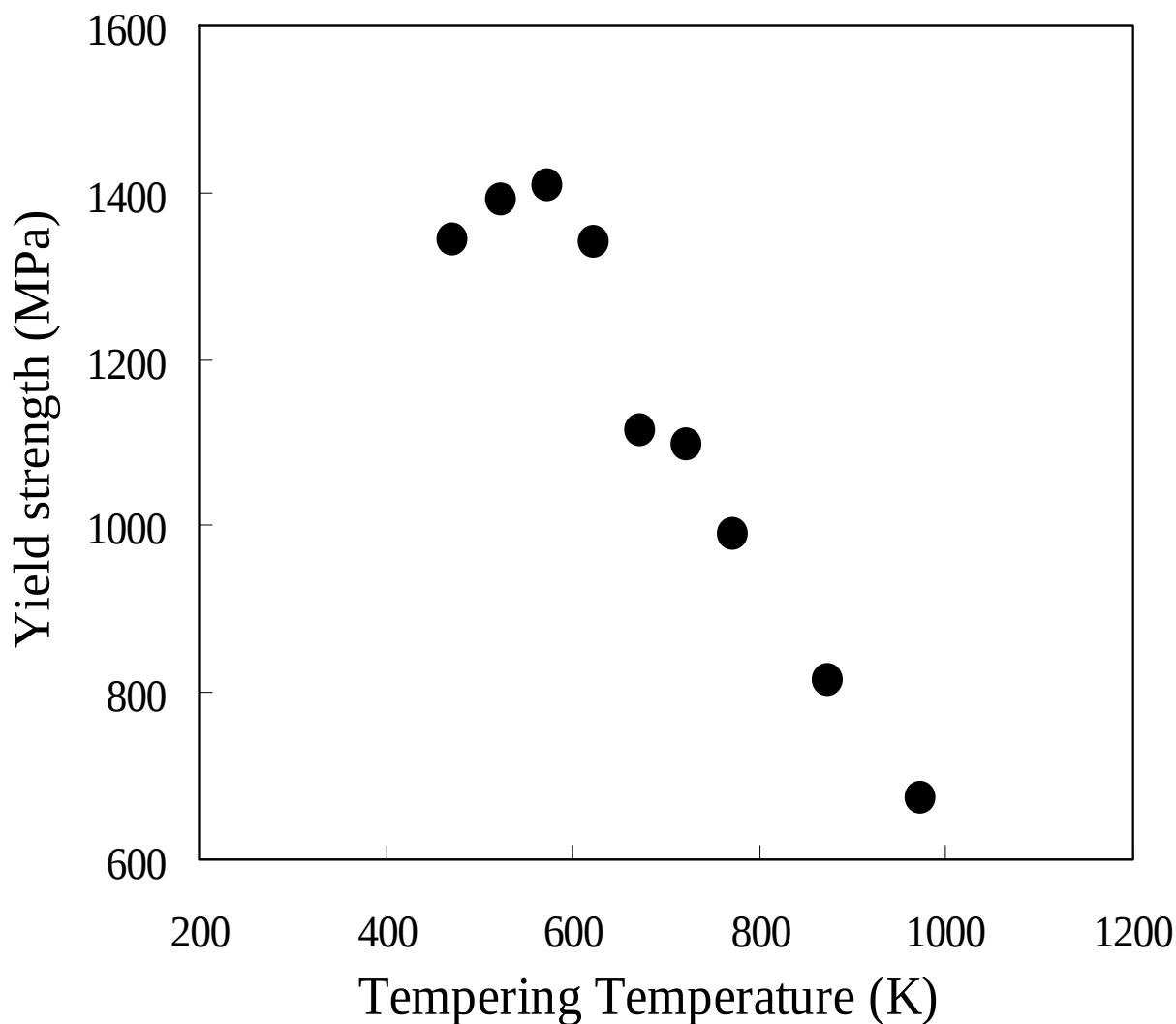


Fig. 3-5. Relationship between yield strength and tempering temperature in ASTM A490 steels.

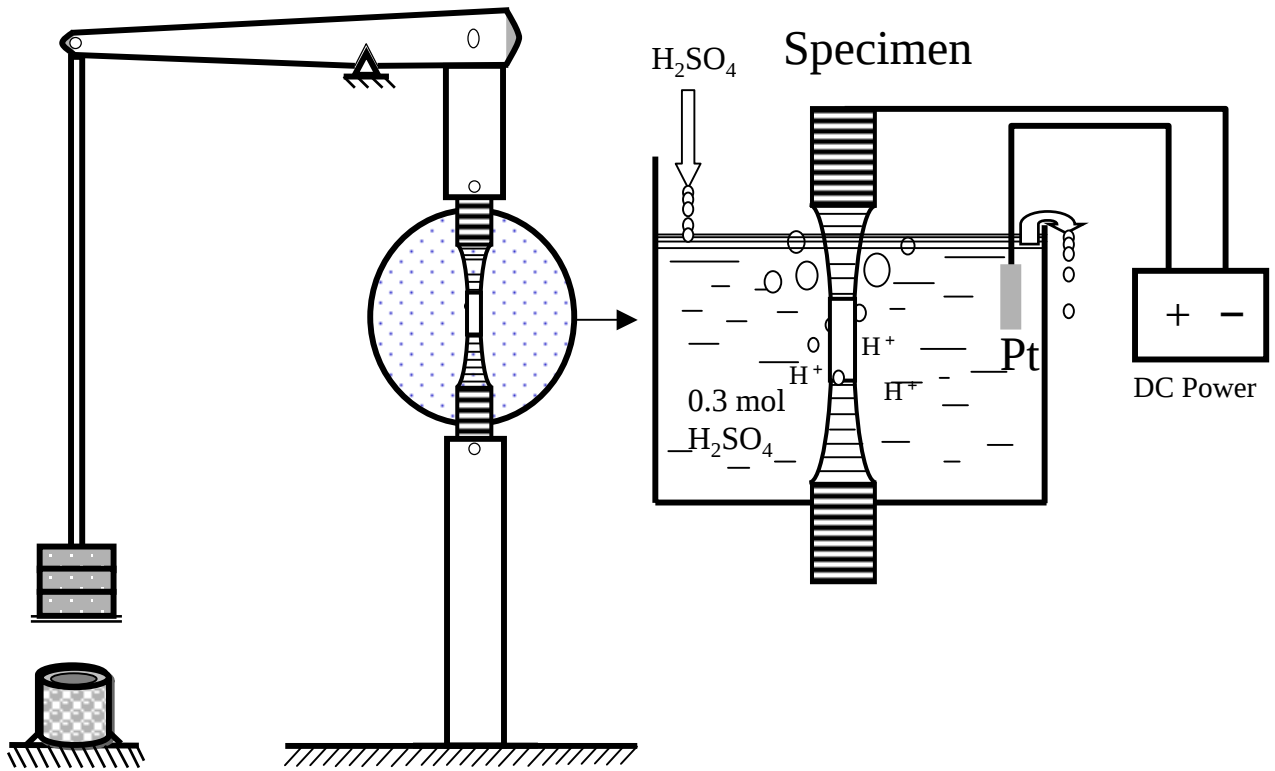


Fig. 3-6. Three-ton-creep test apparatus and hydrogen charge by cathode electrolysis method in sulfate solution.

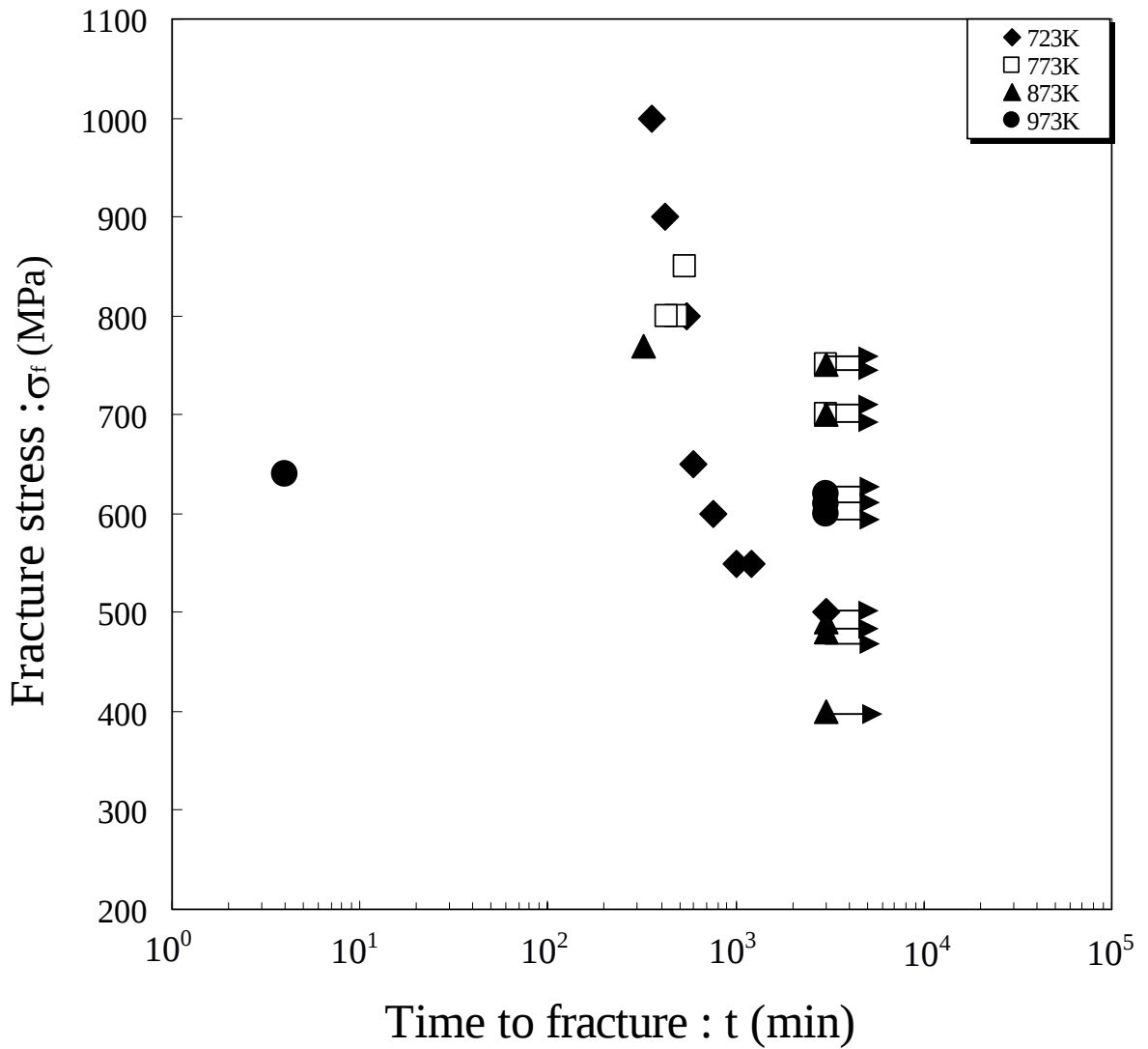


Fig. 3-7. Relationship between fracture stress and time to fracture under delayed fracture test of ASTM A490 steels.

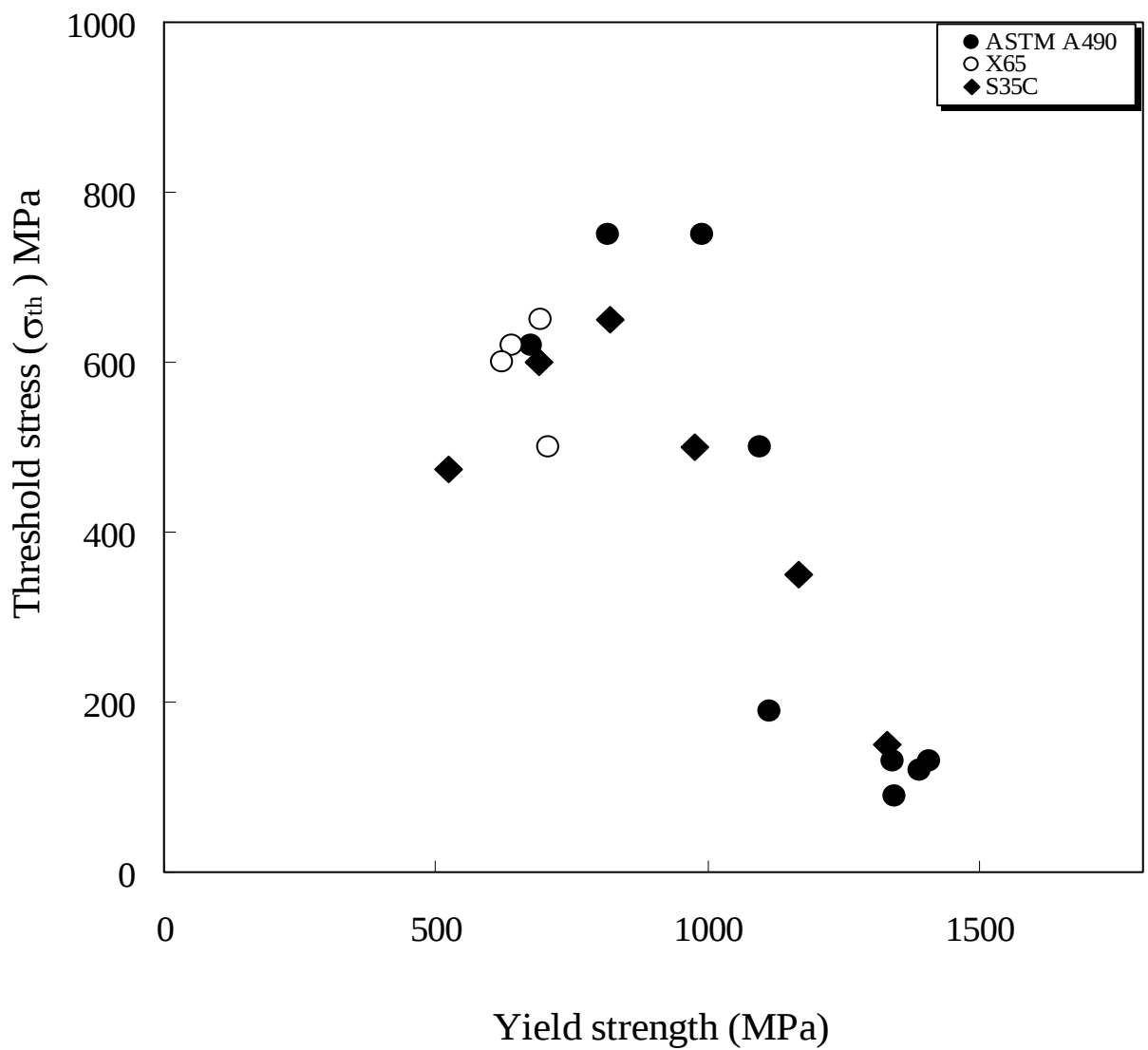


Fig. 3-9. Relationship between threshold stress and yield strength for various kinds of steels.

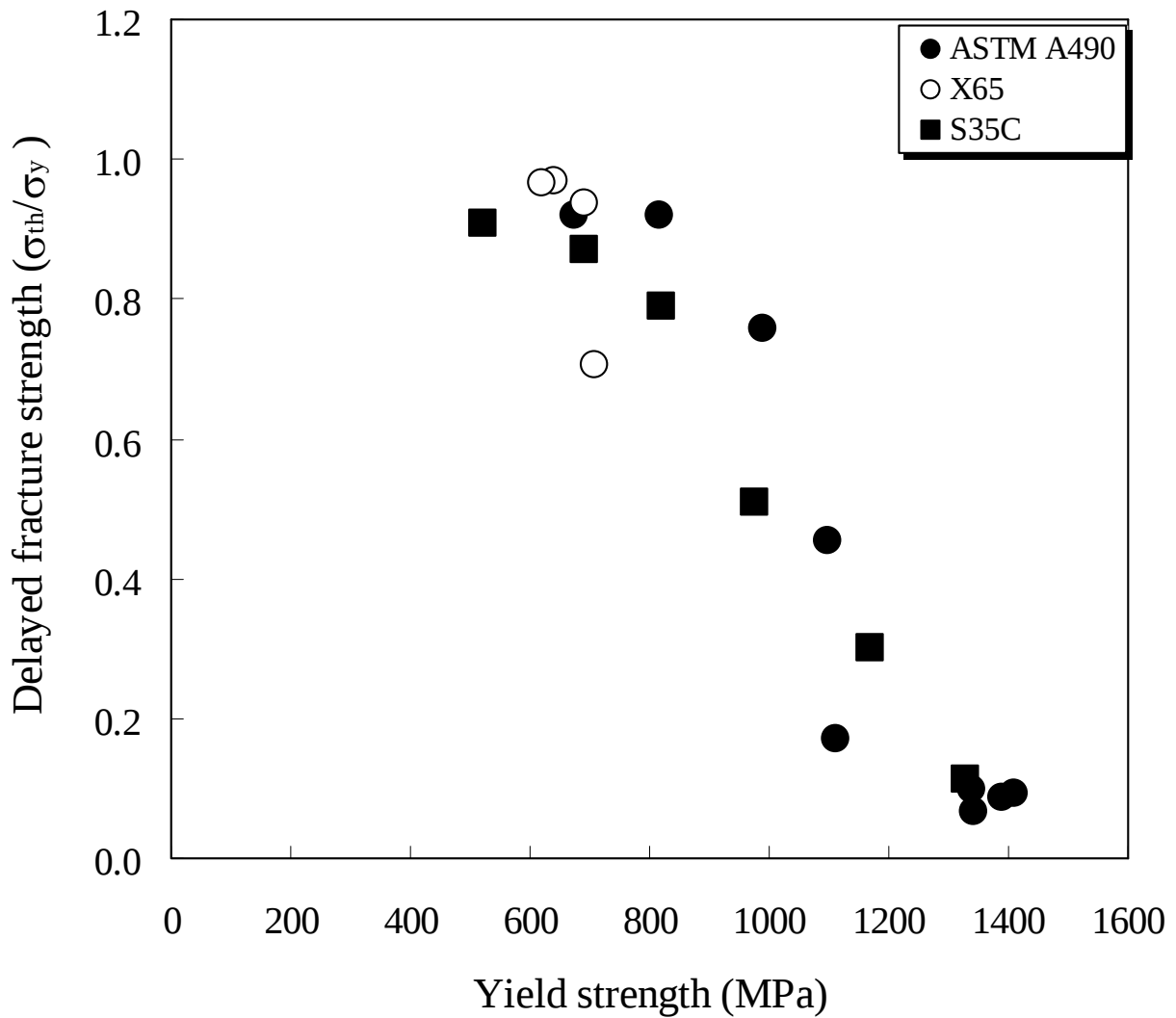
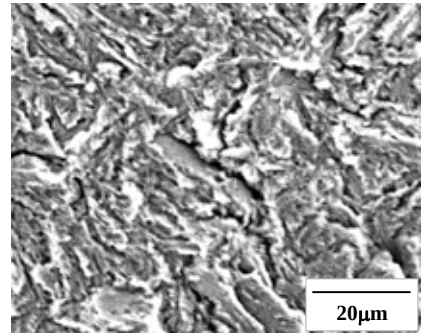
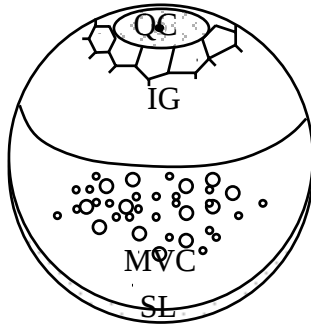
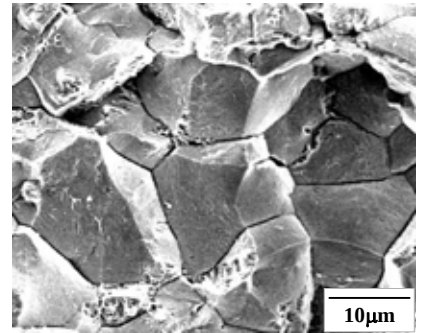


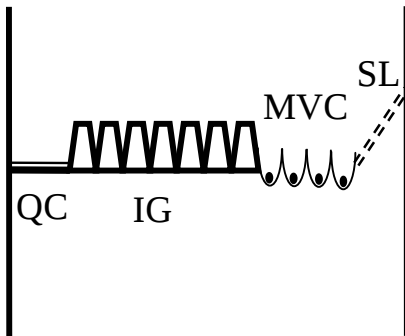
Fig. 3-10. Relationship between delayed fracture strength and the yield strength for various kinds of steels.



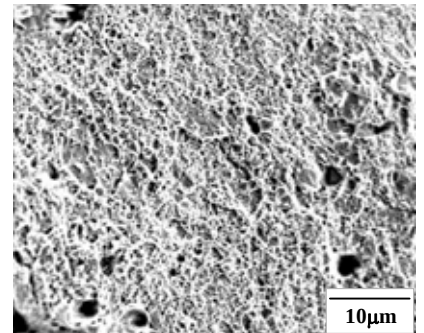
QC facet



IG facet

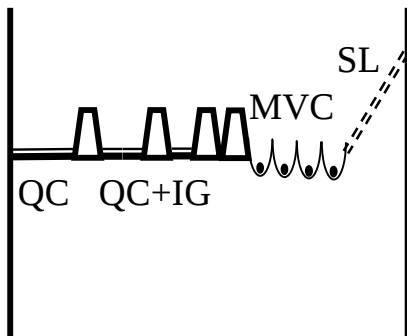


(a) High strength steel

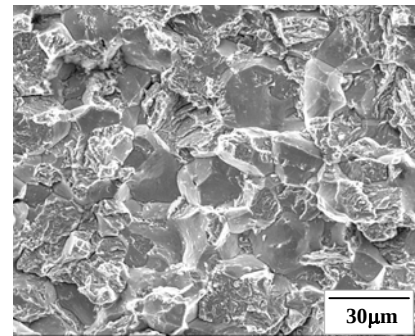


MVC facet

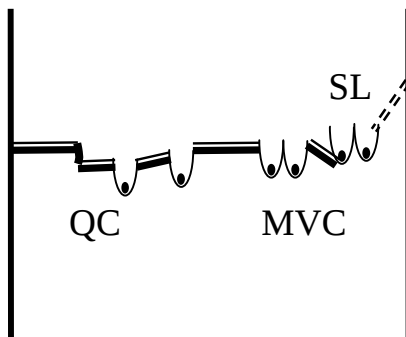
Fig. 3-11-(a). SEM fractographs and morphological characteristics of the fracture surface in high strength steels subjected to delayed fracture test.



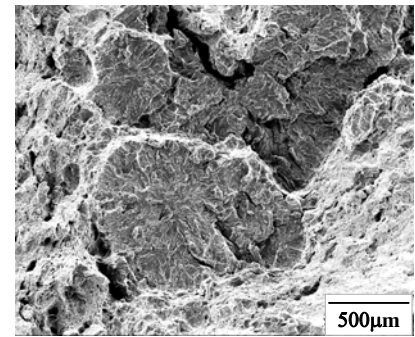
(b) *Medium strength steel*



QC+IG facet
 $\sigma_f = 650\text{MPa}$, $t = 5,893\text{min}$

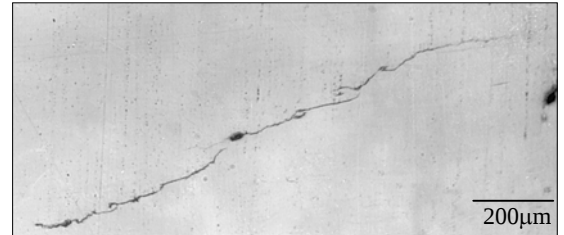
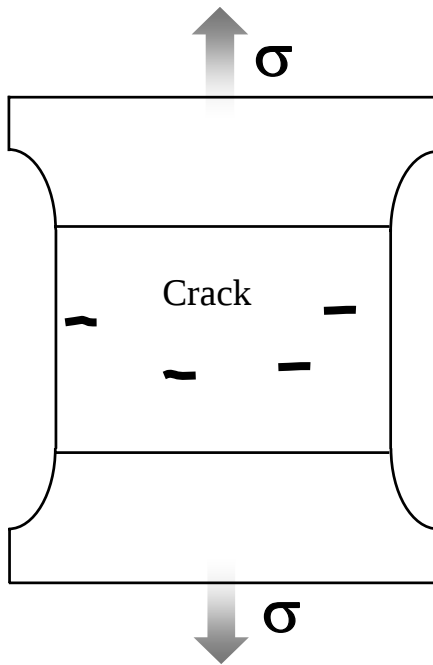


(c) *Low strength steel*

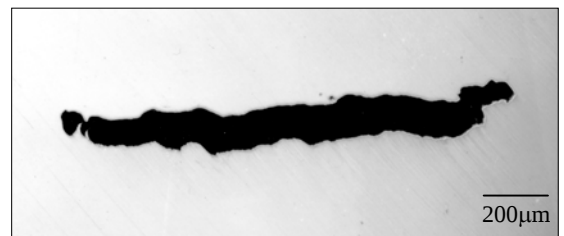


QC facets
 $\sigma_f = 490\text{MPa}$, $t = 6,150\text{min}$

Fig. 3-11-(b). SEM fractographs and morphological characteristics of the fracture surface in medium and low strength steels subjected to delayed fracture test.



(a) High strength steel (ASTM 490)
 $\sigma = 90 \text{ MPa}$, $t = 10,000$ minutes



(b) Low strength steel (API X65)
 $\sigma = 500 \text{ MPa}$, $t = 10,000$ minutes

Fig. 3-12. Difference in crack tip morphologies between low and high strength steels (API X65 and ASTM A490) in optical micrograph taken at the cross section.

(Delayed fracture tests were discontinued at 10,000 minutes.)

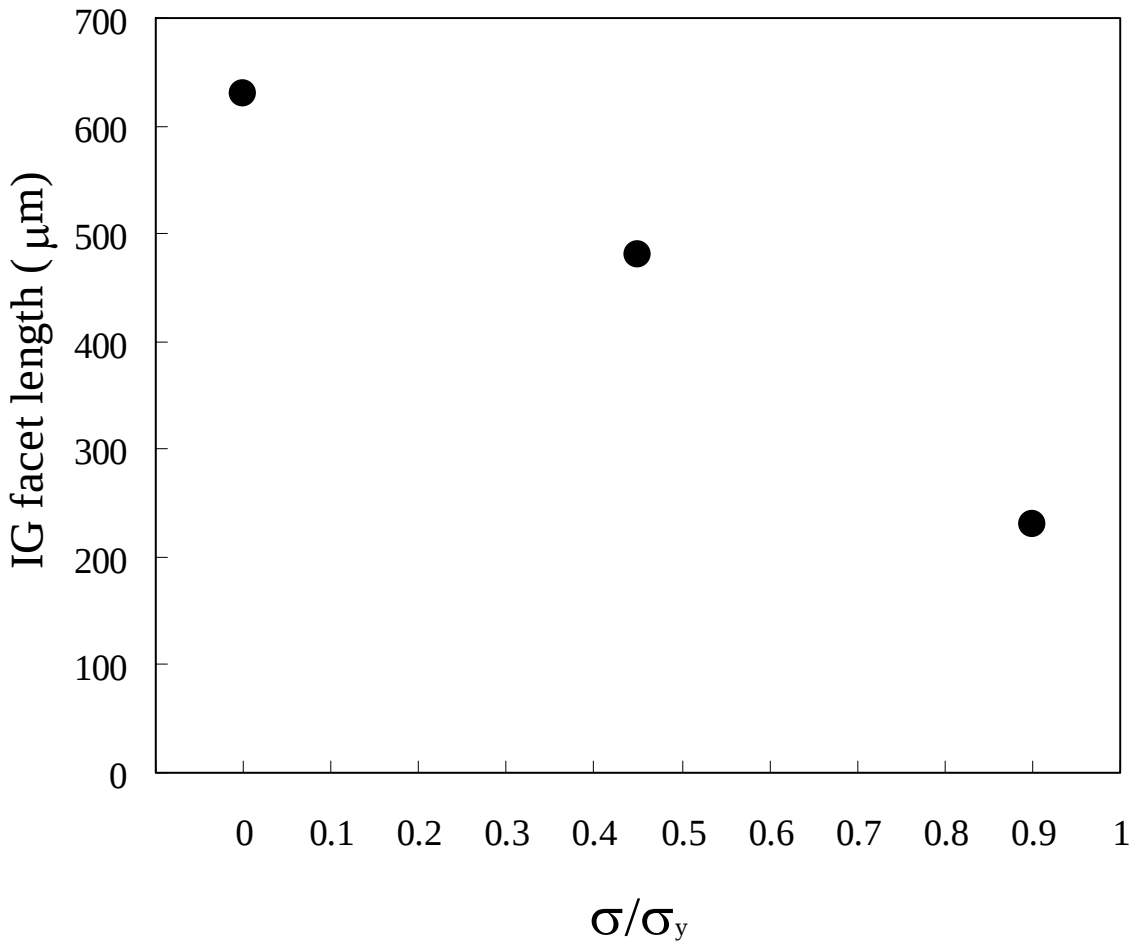


Fig. 3-13. Relationship between IG facet length and applied preload stress (σ/σ_y) in ASTM A490 steels.

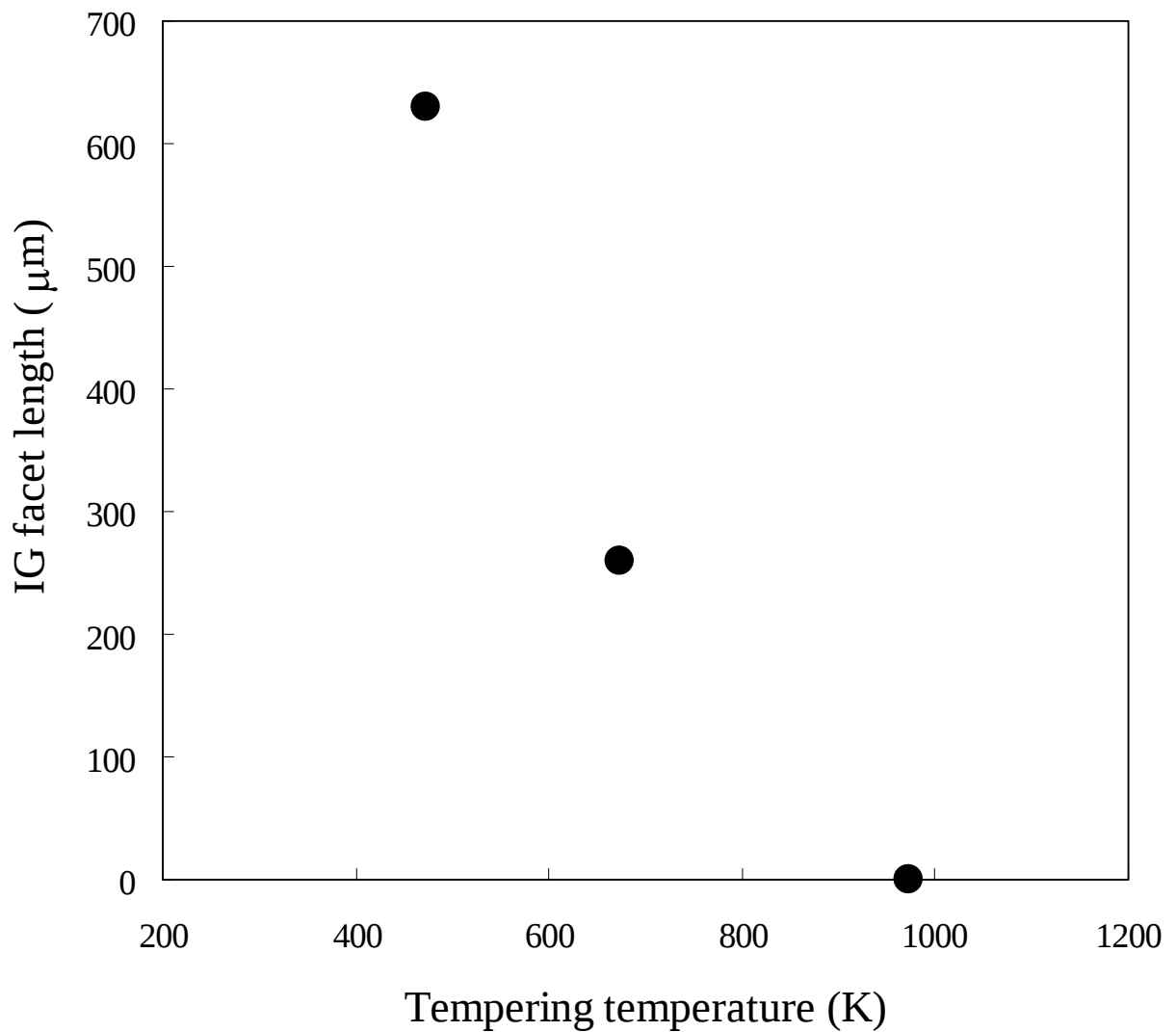


Fig. 3-14. Relationship between IG facet length and tempering temperature in ASTM A490 steels. ($\sigma_f=400\text{MPa}$)

Table 4-1. Chemical compositions of specimens

wt%

Materials	C	Si	Mn	P	S	Cr	Mo	Fe
API X80	0.08	0.22	1.85	0.007	0.002	---	0.12	Bal
Filler Metal	0.06	0.47	1.61	0.006	0.003	0.5	0.58	Bal

Table 4-2. MAG welding conditions

WELDING	Gas (Ar/CO ₂)	Average of heat input amount	Temperature among W- electrodes (K)	Bevel angle	Diameter of filler	Numbers of W-electrode
MAG welding	80/20%	1.15(kJ/mm)	Less then 323	40 °	1.2mm	6

Table 4-3. Mechanical Properties of specimens

Materials	0.2% Proof Strength (MPa)	Tensile Strength (MPa)	Vickers Hardness (p=10kg, 30points)	Elongation percentage
Specimen B (API X80)	610	770	240	20%
Specimen C (Weld metal)	860	920	310	23%
Specimen D (Weld metal without marked welding defects)	531	676	231	22%

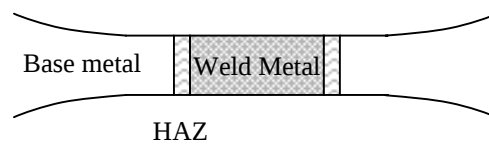
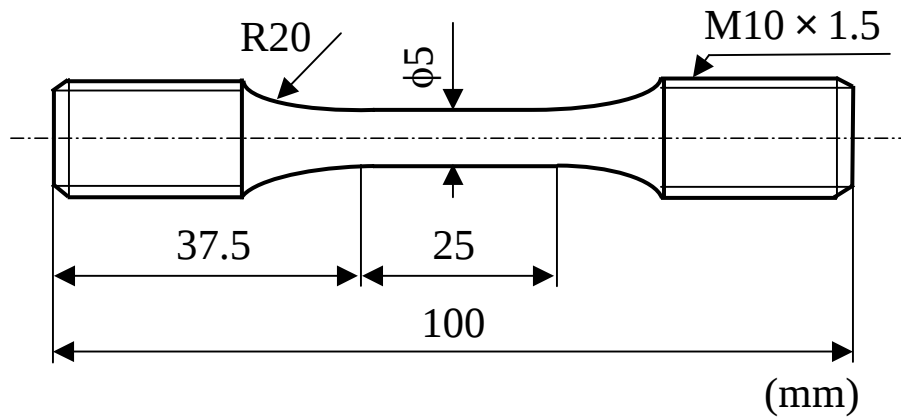
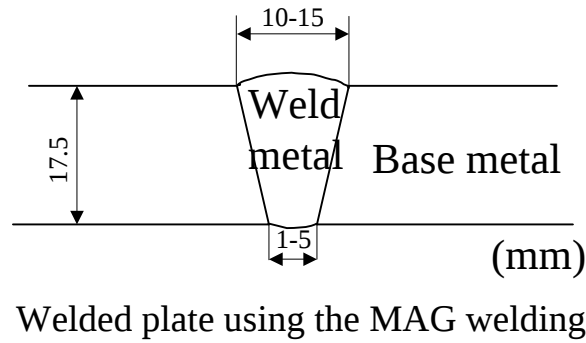


Fig. 4-1. Shape and dimensions of the welded plate and the unnotched specimen which consist of three microstructural components; the base metal, the HAZ, and the weld metal. (Specimen A)

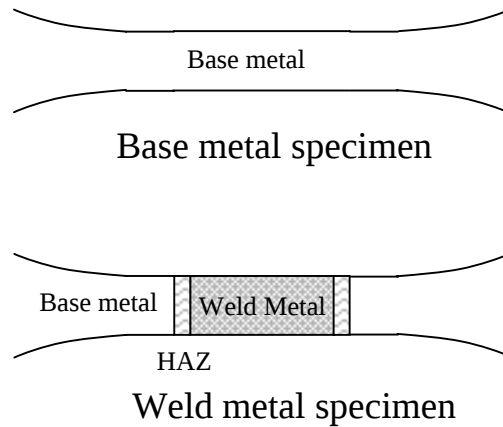
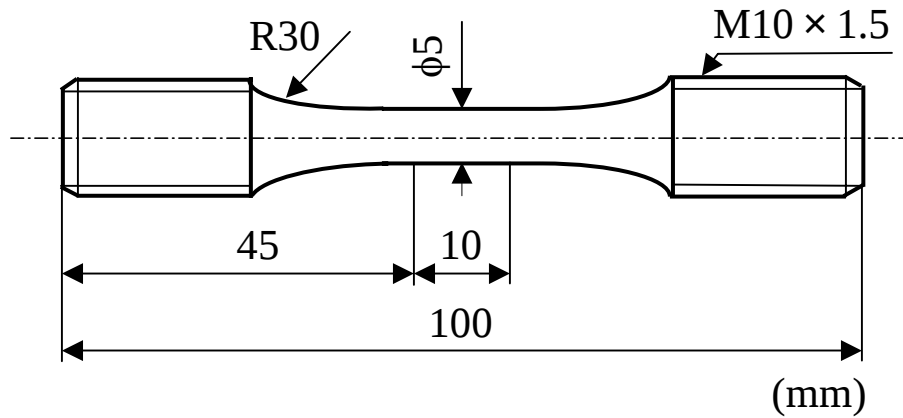


Fig. 4-2. Shape and dimensions of unnotched specimens which consists of a single microstructural component; the base and the weld metals, respectively. (Specimens B, C and D)

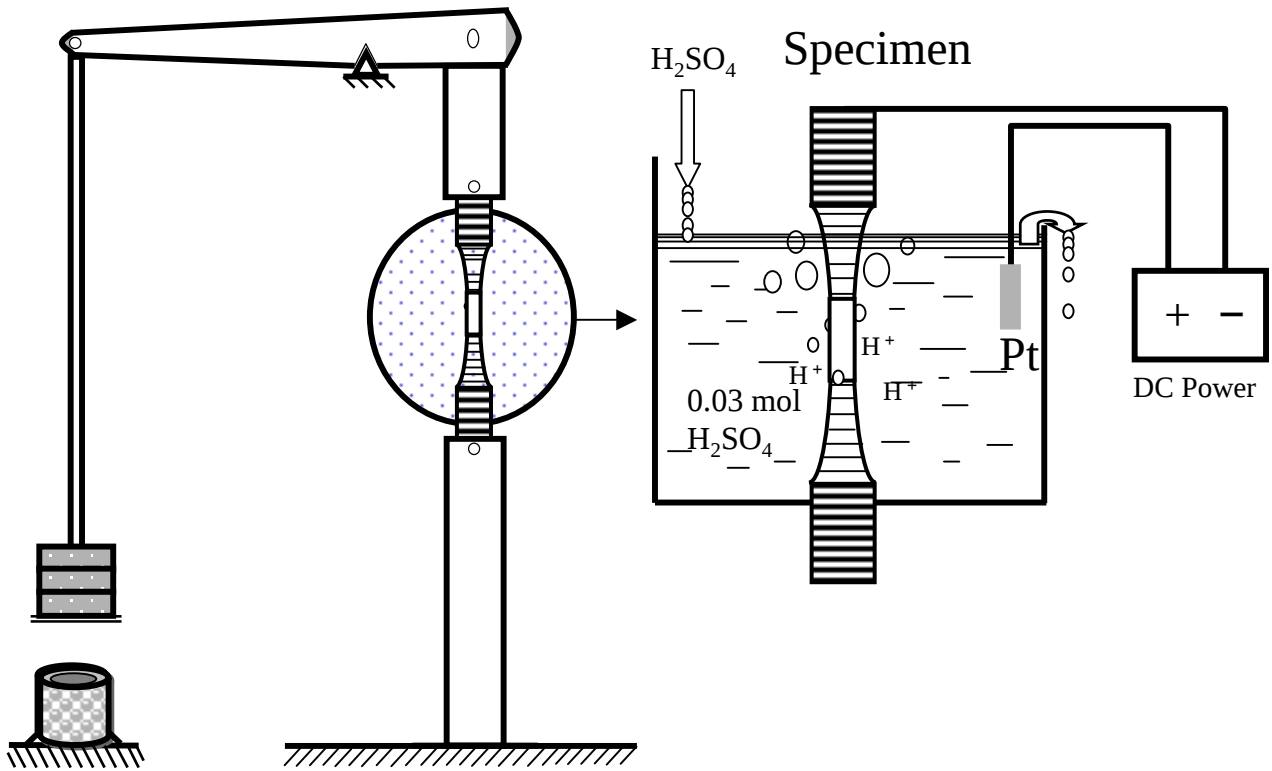


Fig. 4-3. Three-ton-creep test apparatus and hydrogen charge by cathode electrolysis method in sulfate solution.

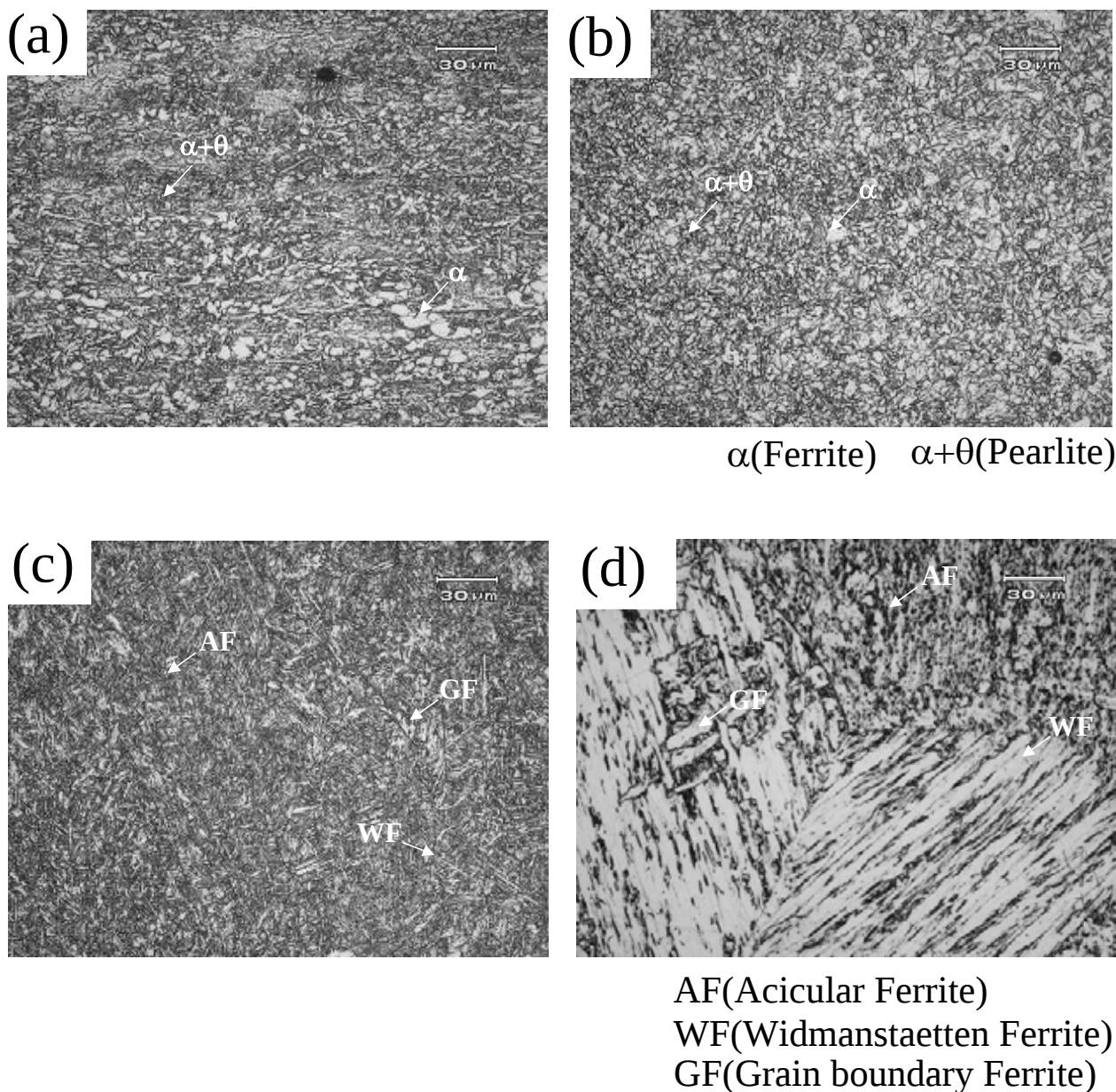


Fig. 4-4. Metallographs showing the base metal, HAZ, and the weld metal of the specimen A: (a) base metal, (b) HAZ, (c) weld metal, (d) weld metal without marked defects due to welding process.

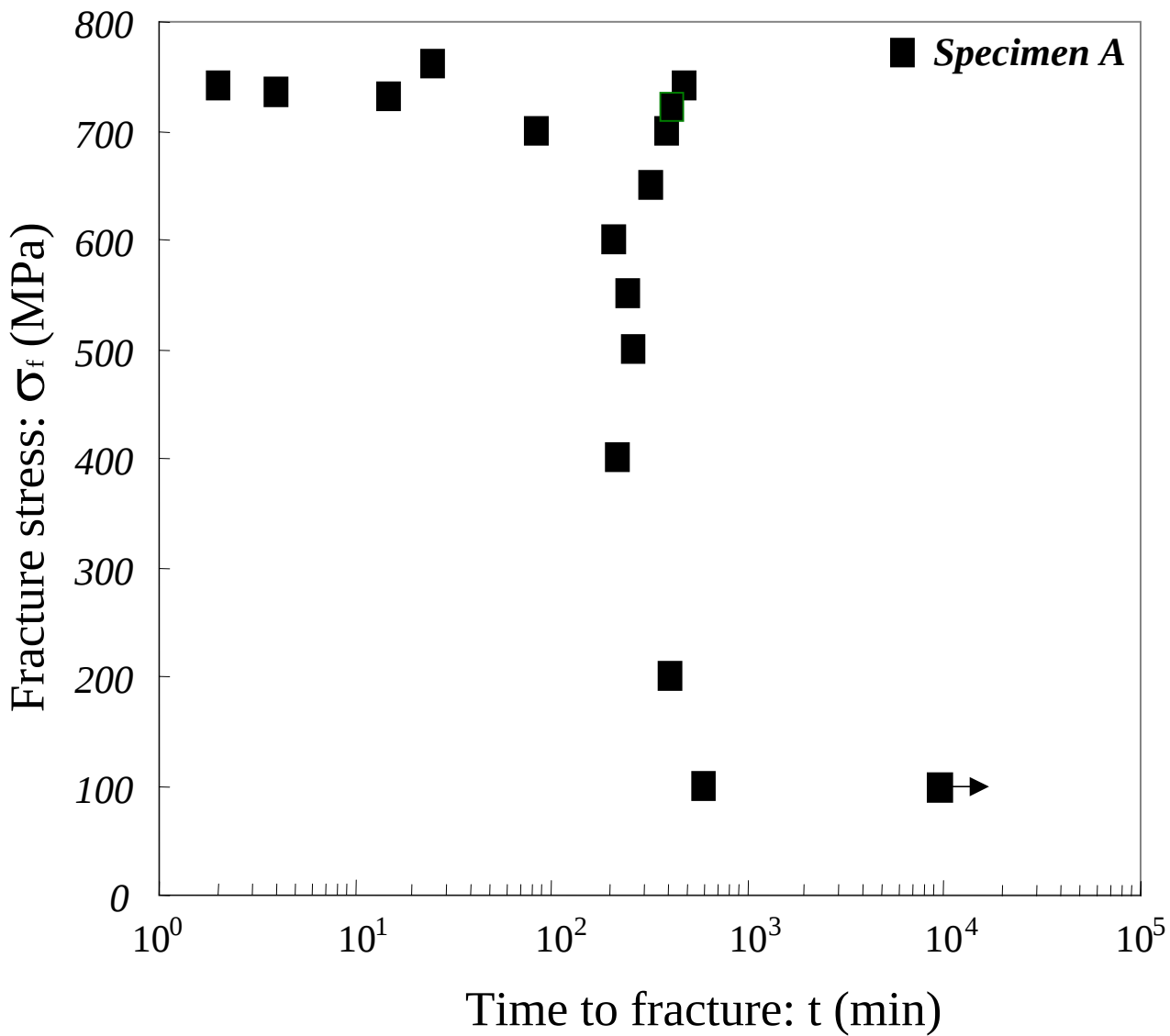
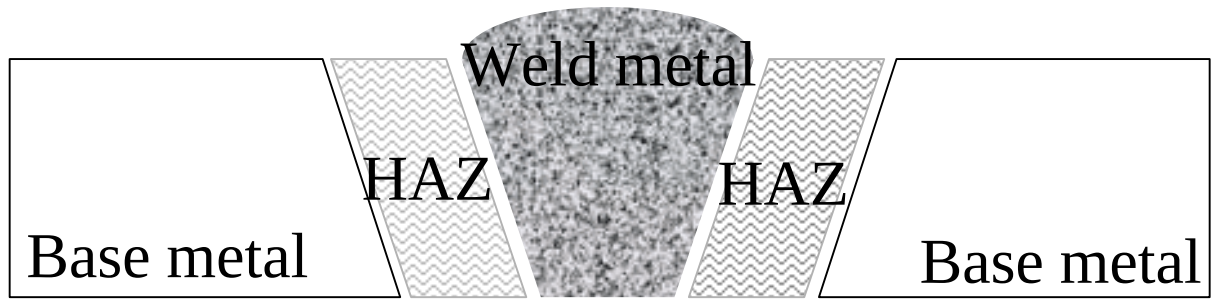
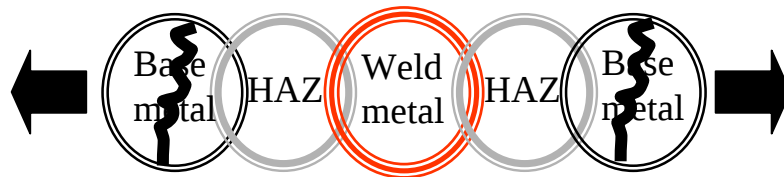


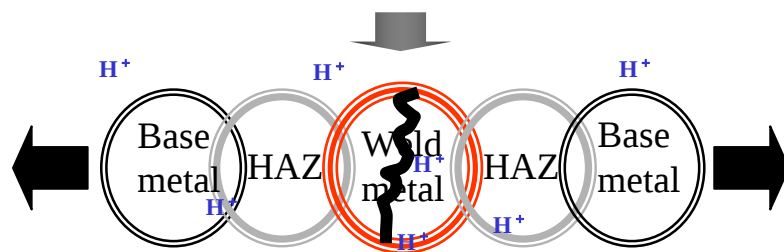
Fig. 4-5. Relationship between fracture stress and time to fracture in delayed fracture of the specimen A.



(a) Welded plate is made by “over-matching” method to prevent the welded joints from static fracture.



(b) Weakest-link concept for the static strength of the welded joints in air



(c) Delayed fracture strength of the welded joints under hydrogen attack

Fig. 4-6. The Weakest-link concept of the specimen A in air and under hydrogen attack.

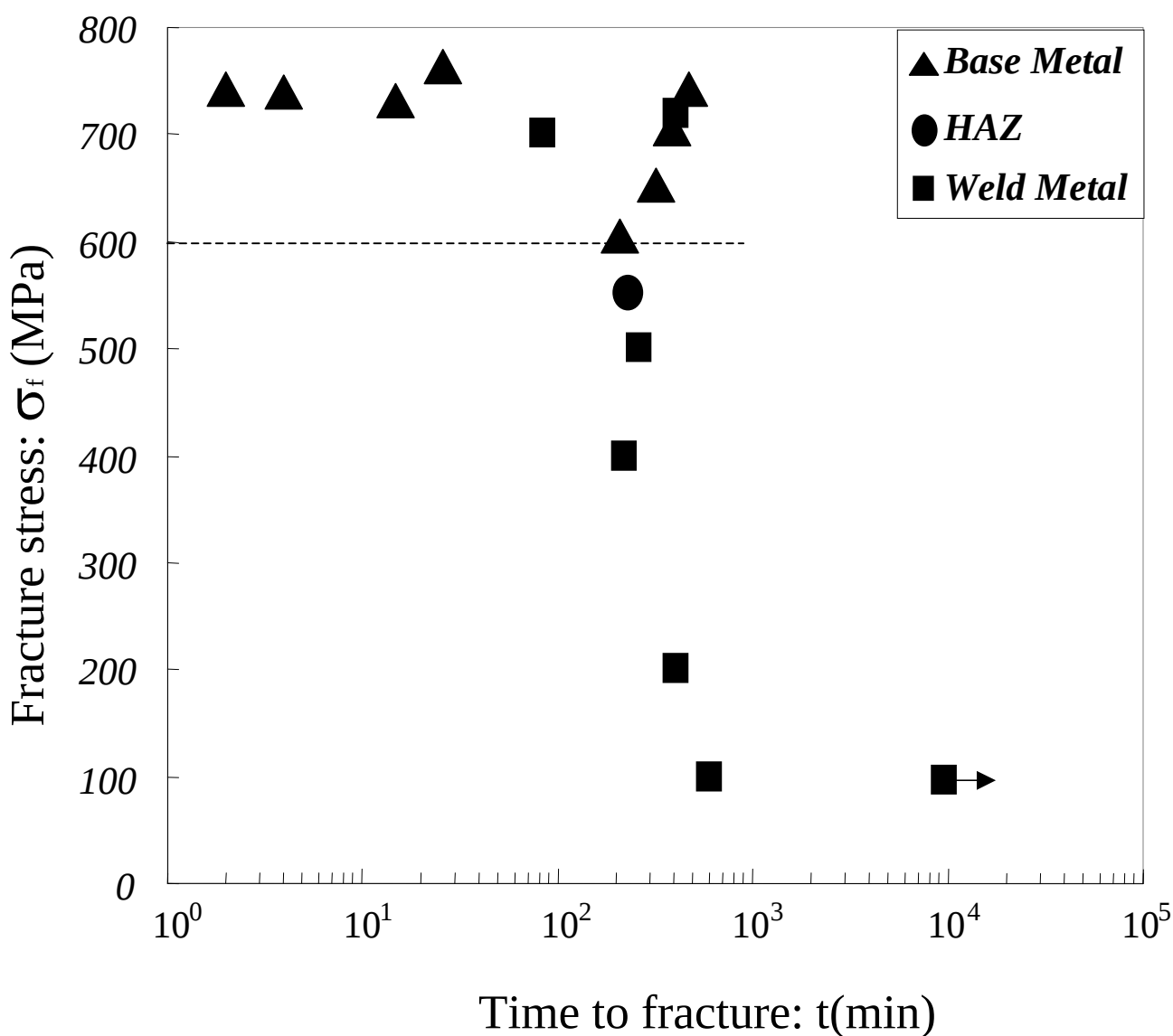


Fig. 4-7. Change of fracture spot according to the levels of applied stress for the specimen A.

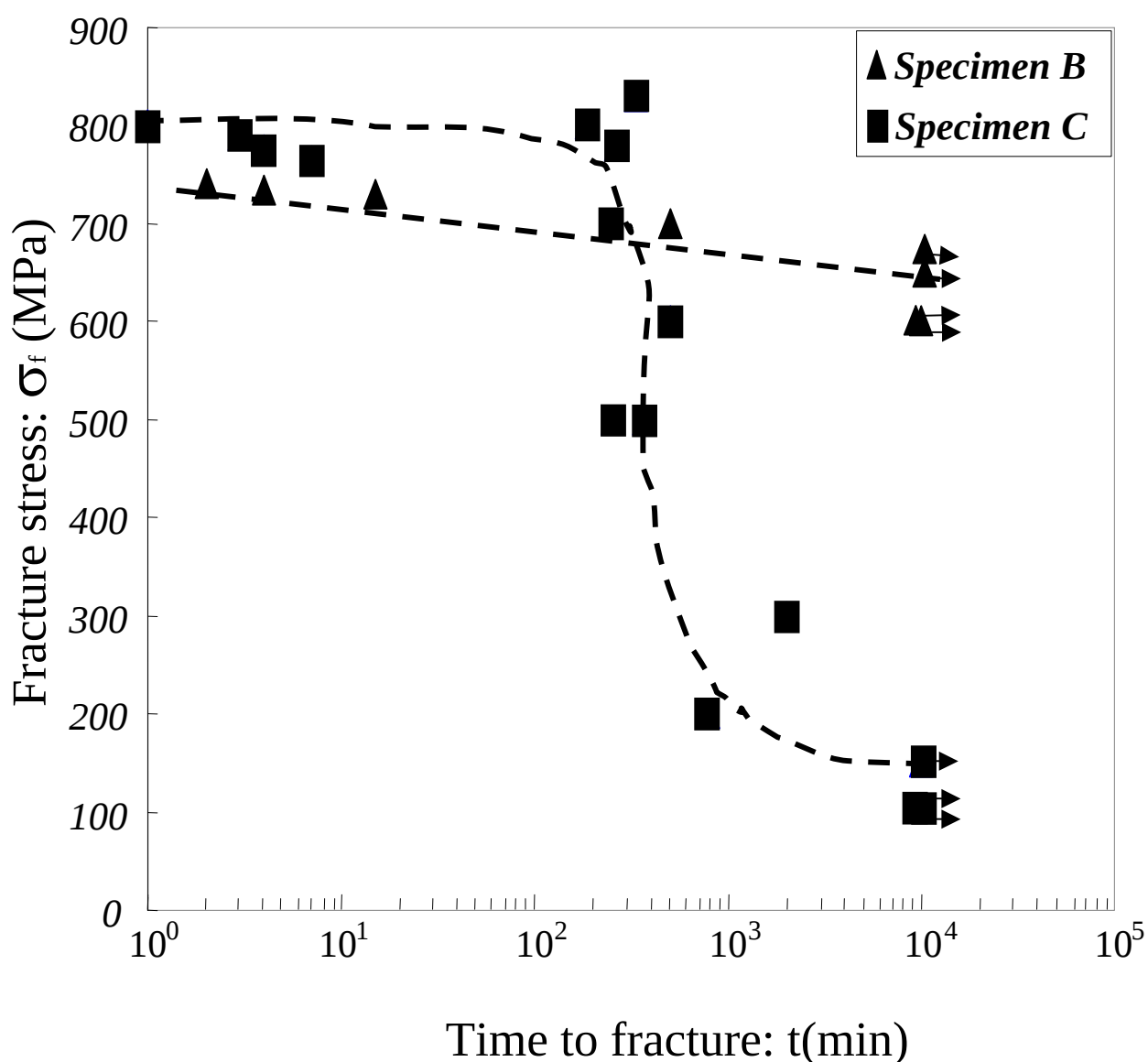


Fig. 4-8. Relationship between fracture stress and time to fracture in delayed fracture of the specimens B and C.

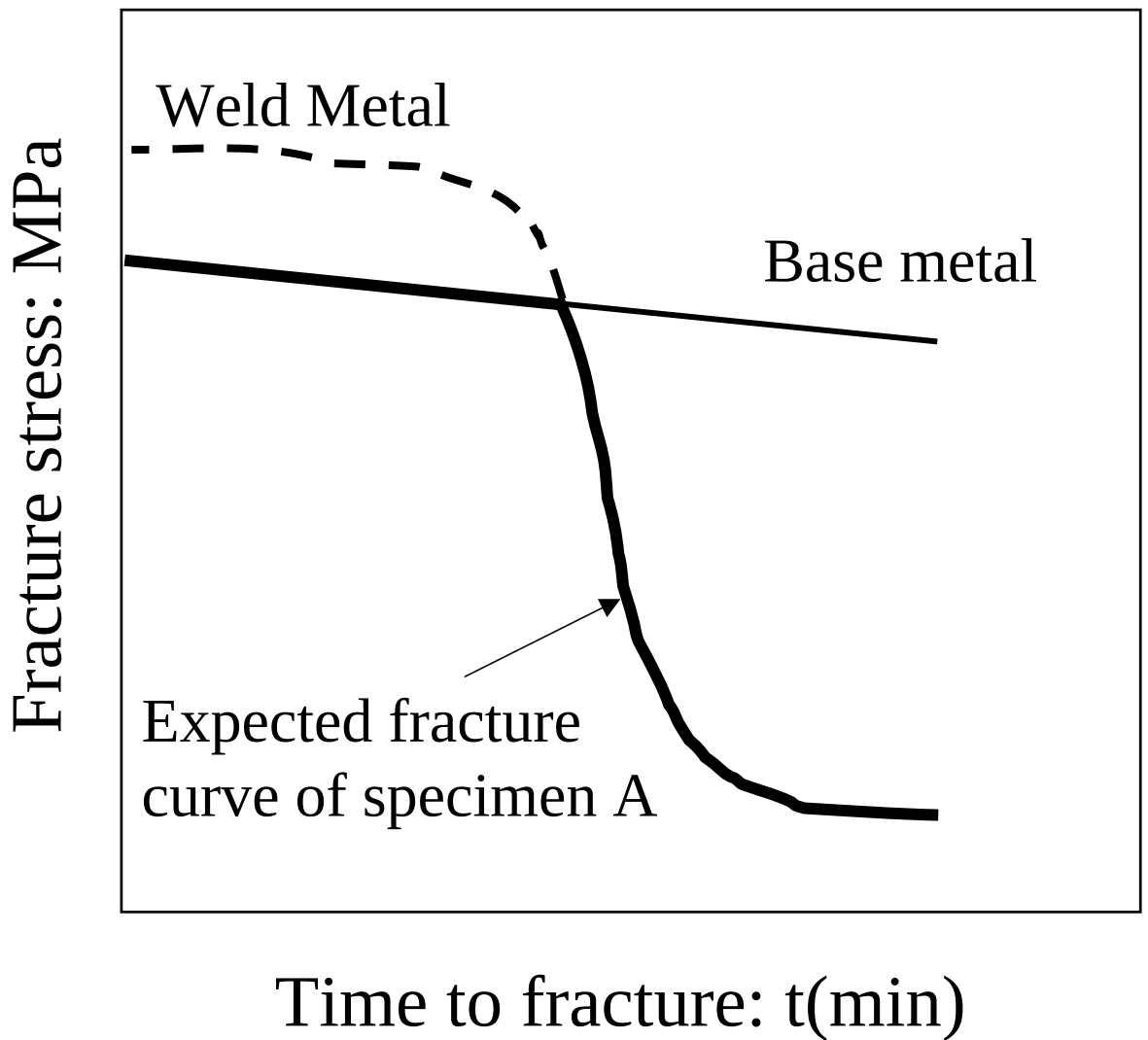


Fig. 4-9. Schematic illustration of synthesized fracture curve of welded joints which consist of the base metal and the weld metal.

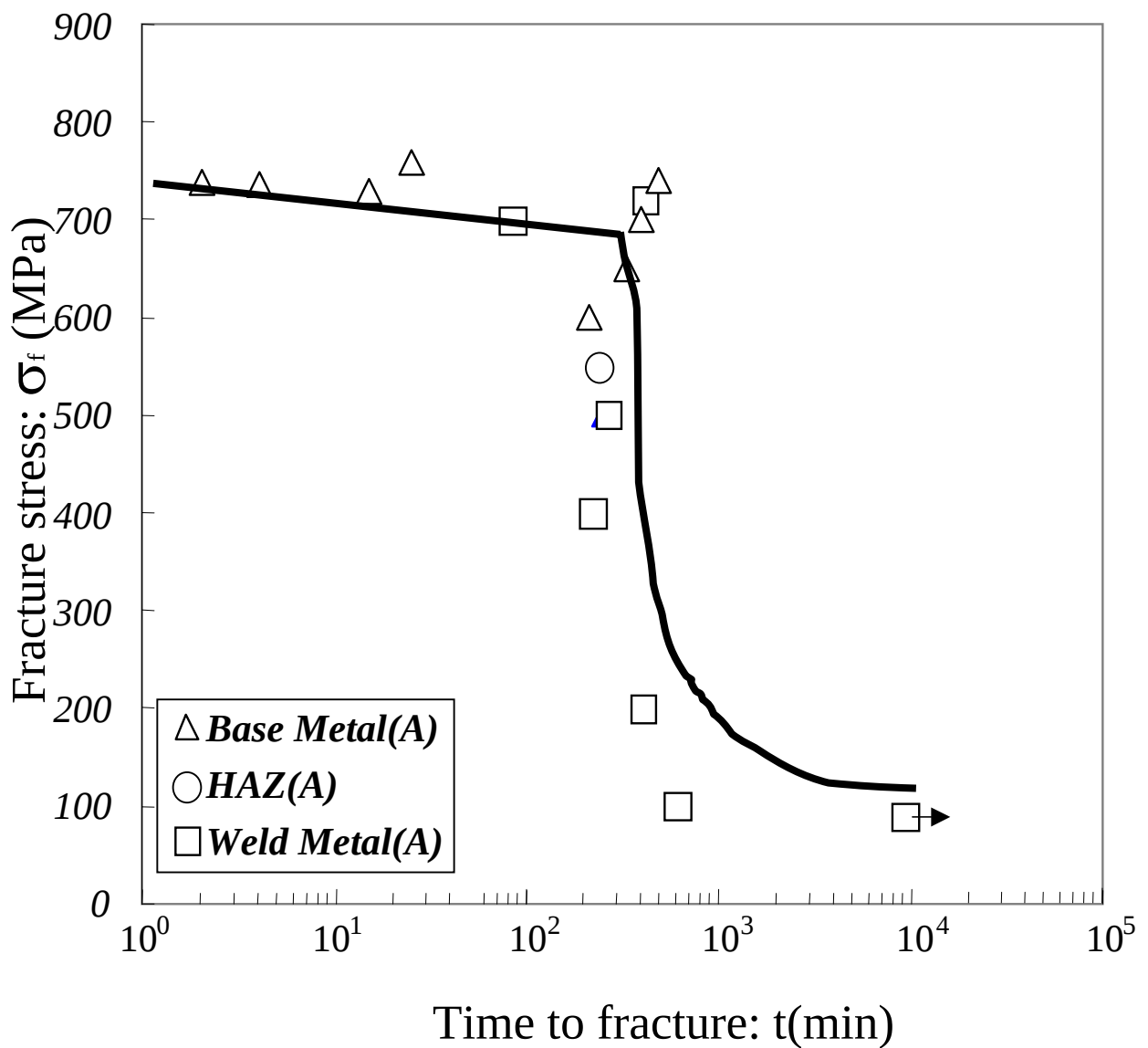


Fig. 4-10. The results of fracture strength of specimen A and expected fracture curve.

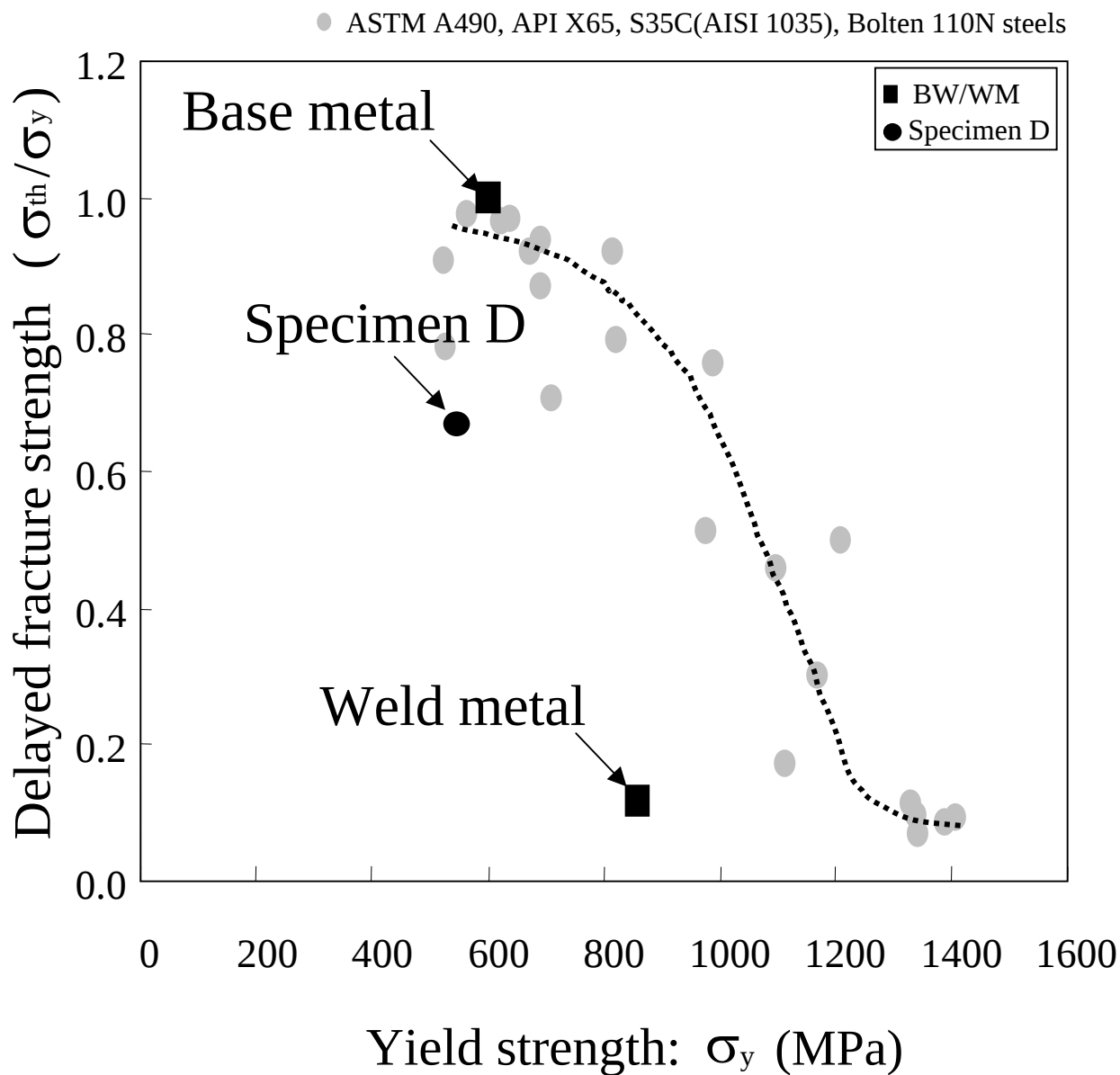
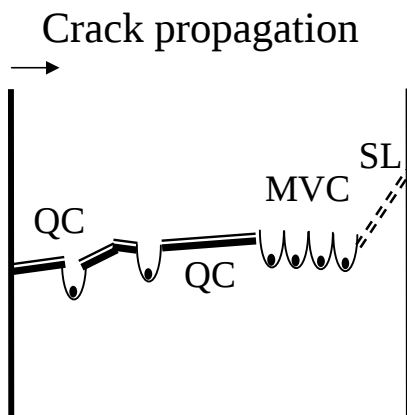
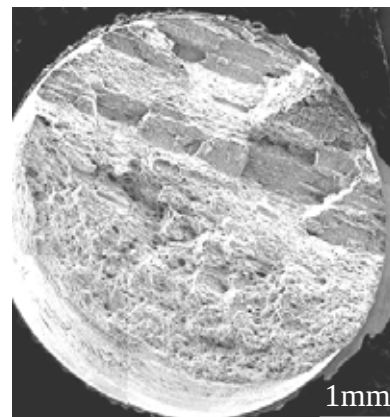


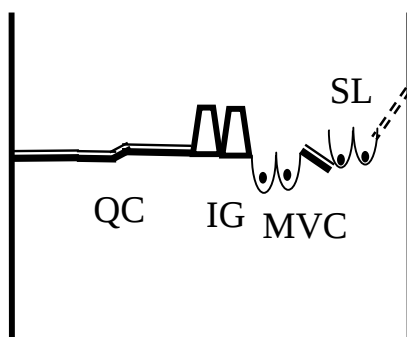
Fig. 4-11. Comparison of the delayed fracture strength of the base and the weld metals with that of carbon steels with a wide range of yield strengths.



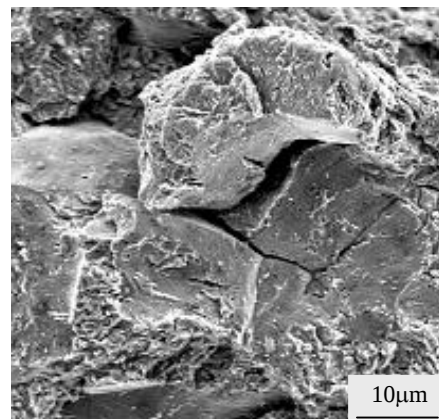
(a) Base metal



$\sigma_f = 700\text{MPa}$, $t = 387\text{min}$



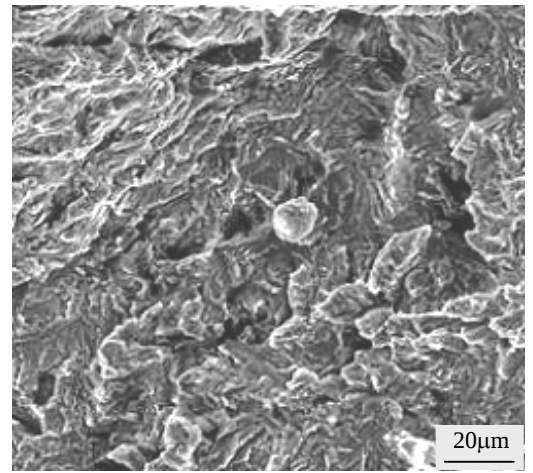
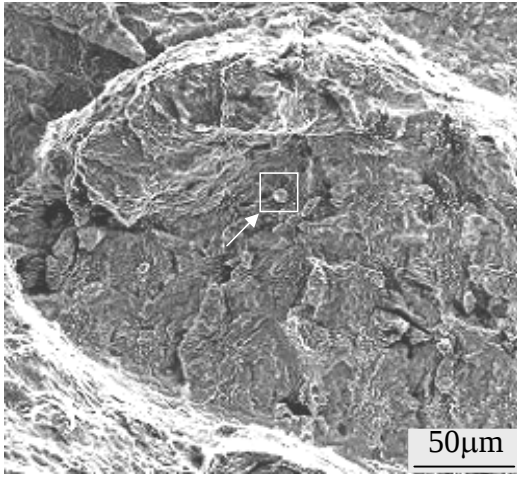
(b) Weld metal



IG facet

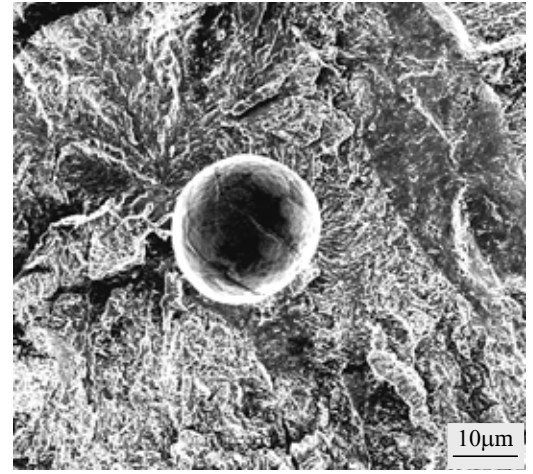
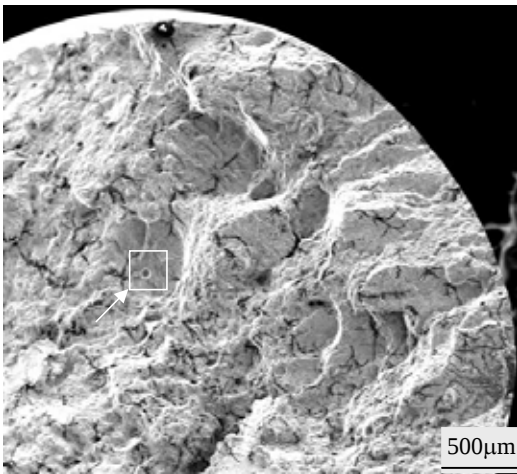
$\sigma_f = 200\text{MPa}$, $t = 784\text{min}$

Fig. 4-12. Morphological characteristics of fracture surface and crack propagation behavior in the base metal and the weld metal.



Non-metallic inclusion

(a) The origin of QC crack in Base Metal ($\sigma_f = 700\text{MPa}$, $t = 387\text{min}$)



Blowhole

(b) The origin of QC crack in Weld Metal ($\sigma_f = 650\text{MPa}$, $t = 40\text{min}$)

Fig. 4-13. The initiation sites of crack in crack propagation process of the base metal and the weld metal.

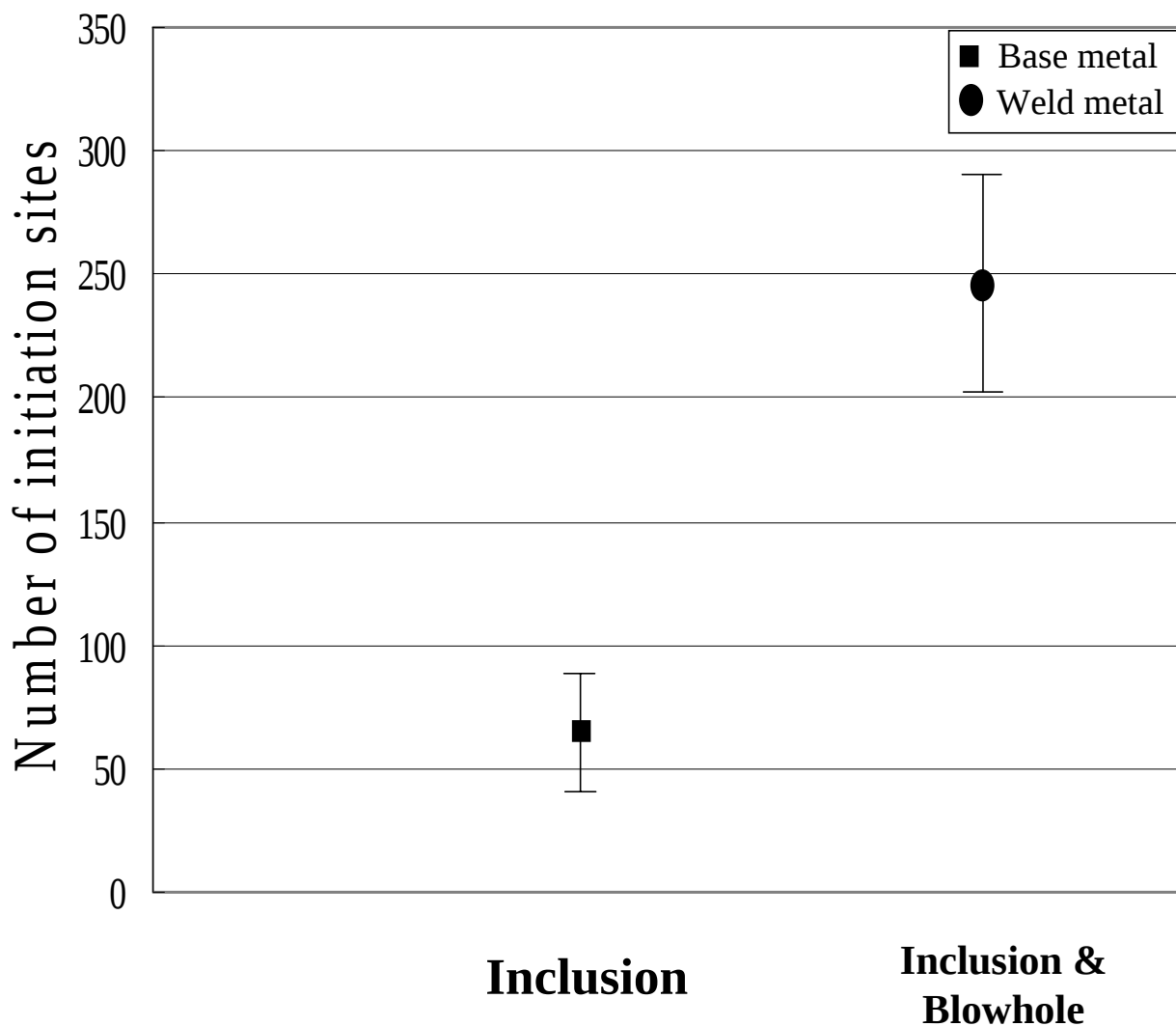
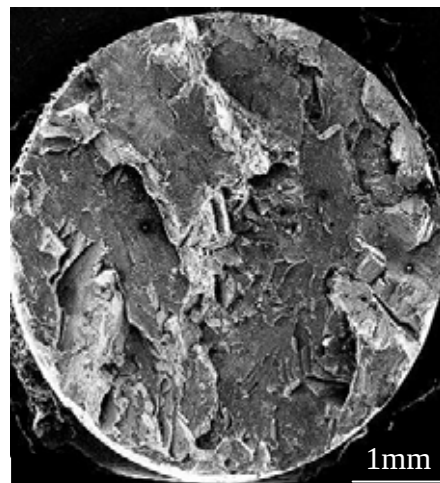
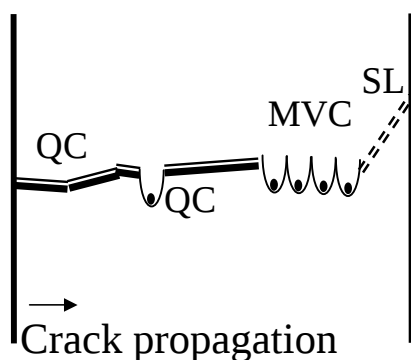
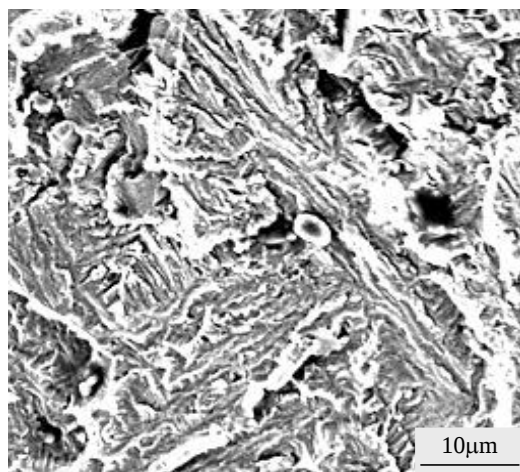
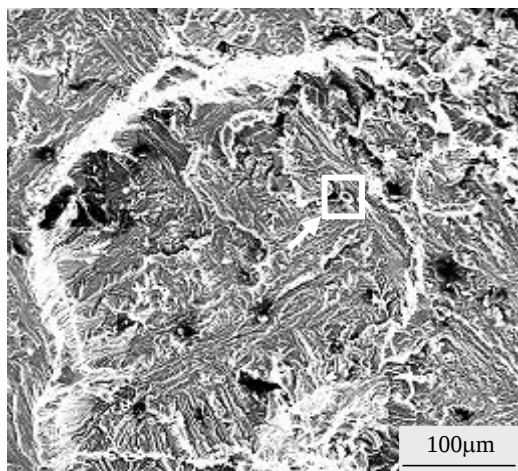


Fig. 4-14. Relationship between the number of initiation sites as the QC cracks and non-metallic inclusions, blowholes in the base and the weld metals



(a) Crack propagation morphology and SEM photography ($\sigma_f = 500\text{MPa}$, $t = 809\text{min}$)



Non-metallic inclusion

(b) An initiation of QC crack ($\sigma_f = 400\text{MPa}$, $t = 1921\text{min}$)

Fig. 4-16. Characteristics of fracture surface and crack propagation behavior and initiation sites of QC cracks in weld metal without marked defects due to welding process.(Specimen D)