

Effect of Intergranular Ferrite on Hydrogen Delayed Fracture Resistance of High Strength Boron-added Steel

Ji Soo Kim^a, Kyung-Tae Park^b, Duklak Lee^c, Chong Soo Lee^a

^aDepartment of Materials Science and Engineering
Pohang University of Science and Technology, Pohang 790-784, Korea

^bDivision of Advanced Materials Science and Engineering
Hanbat National University, Daejeon 305-719, Korea

^cTechnical Research Laboratory, POSCO, Pohang 790-785, Korea

ABSTRACT

In this study, the effect of intergranular ferrite volume fraction on the hydrogen delayed fracture (HDF) resistance of high strength boron-added steel was investigated. For this purpose, constant loading tests were conducted on cathodically charged specimens having the three intergranular ferrite volume fractions, i.e., 0%, 6% and 10%. With the increase of the intergranular ferrite volume fraction, the HDF resistance in boron-added steel was improved. TEM and SEM observations revealed that most of the ferrite grains were located at prior austenite grain boundaries, thereby reducing the susceptible sites for crack nucleation. The fracture mode of steel without having any intergranular ferrite was a type of intergranular fracture. However, the mode changed from intergranular fracture to quasi-cleavage fracture with the increase of the intergranular ferrite volume fraction. Thermal desorption analysis evidenced that the grain boundaries were the main trapping sites of diffusible hydrogen.

1. INTRODUCTION

In the steel industry, suppression of the delayed fracture of high strength steels becomes very important subject because the hydrogen susceptibility increases with the increase of strength of steels [1]. Despite considerable researches over several decades, the mechanisms of delayed fracture for high strength steels have not been fully understood yet [2]. So far, many efforts have been made to improve the hydrogen delayed fracture resistance either by the addition of alloying elements or by the control of microstructure [3-5]. It has been found that propagation of cracks due to hydrogen embrittlement is the

intergranular fracture. Therefore, it is reasonable to think that if the soft phases such as ferrite exist at the grain boundaries, the crack propagation would be effectively retarded. However, the effect of the presence of intergranular ferrite on delayed fracture of high strength steels have rarely been investigated.

The boron-added steels with the tensile strength level of 1100 MPa are commonly used for high strength bolts in quenched and tempered condition. However, they show high susceptibility to hydrogen delayed fracture when treated to high strength levels [6]. The purpose of the present study is, therefore, to investigate the effect of intergranular ferrite on hydrogen delayed fracture resistance of a boron-added steel with the strength level of 1100 MPa.

2. EXPERIMENTAL PROCEDURES

The chemical composition of the present boron-added steels used is listed in Table 1.

Table 1. The chemical composition of the boron-added steel used in this study.

Element	C	Si	Mn	P	S	Al	B	Ti	Cr	N	O
Wt. %	0.20	0.056	0.1	0.004	0.004	0.04	0.004	0.04	0.317	43	30

Hot rolled bars with a diameter of 11mm were quenched and tempered with various conditions to produce different amount of ferrite phase. Specimens were quenched into oil after heat treating at the temperature ranges of 770°C ~ 890°C for 1 hr, and subsequently tempered at 450°C for 2 hrs. Tensile and hardness tests were carried out to measure the strength level of the microstructures produced. For the constant loading test, the circumferentially notched round bar specimens with a notch root radius of 0.1mm (i.e., a stress concentration factor of 4.9) were used. Constant loading tests were carried out up to 150 hours with the stress ratios (applied stress/notch tensile strength) of 0.5 ~ 0.9

Hydrogen was introduced into the specimens by electrochemical pre-charging in 4% NH₄SCN solution for 48 hrs with the current density of 2 A/m². After hydrogen charging, the specimens were coated with cadmium to prevent hydrogen desorption, and

then the specimens were kept at ambient temperature for 24 hours to homogenize the hydrogen distribution. After constant loading test, the specimens were immediately put into liquid nitrogen to prevent hydrogen release, and kept until removal of the cadmium coating for hydrogen measurement by Thermal Desorption Analysis (TDS).

The hydrogen content was measured using TDS at a heating rate of 300K/h. Other heating rates were also used for determining the activation energy of hydrogen desorption according to the method reported by Choo and Lee [7]. TEM and SEM works were performed to investigate the effects of intergranular ferrite on the delayed fracture mode.

3. RESULTS AND DISCUSSION

In this study, the ($\alpha + \gamma$) heat treatment of 870°C, 825°C and 815°C for 1 hr resulted in 0%, 6% and 10% intergranular ferrite volume fractions, respectively, hereafter, the specimens are denoted as A ~ C with the increase of intergranular ferrite volume fraction. The general properties of each specimen are shown in Table 2 and their optical microstructures are shown in Fig. 1.

Table 2. The microstructures and mechanical properties of the specimens

Specimen	Intergranular ferrite volume fraction, %	Mechanical properties		
		YS, MPa	Total elongation, %	Notch TS, MPa
A	0	1068	20	1787
B	6	1095	22	1754
C	10	1083	24	1710

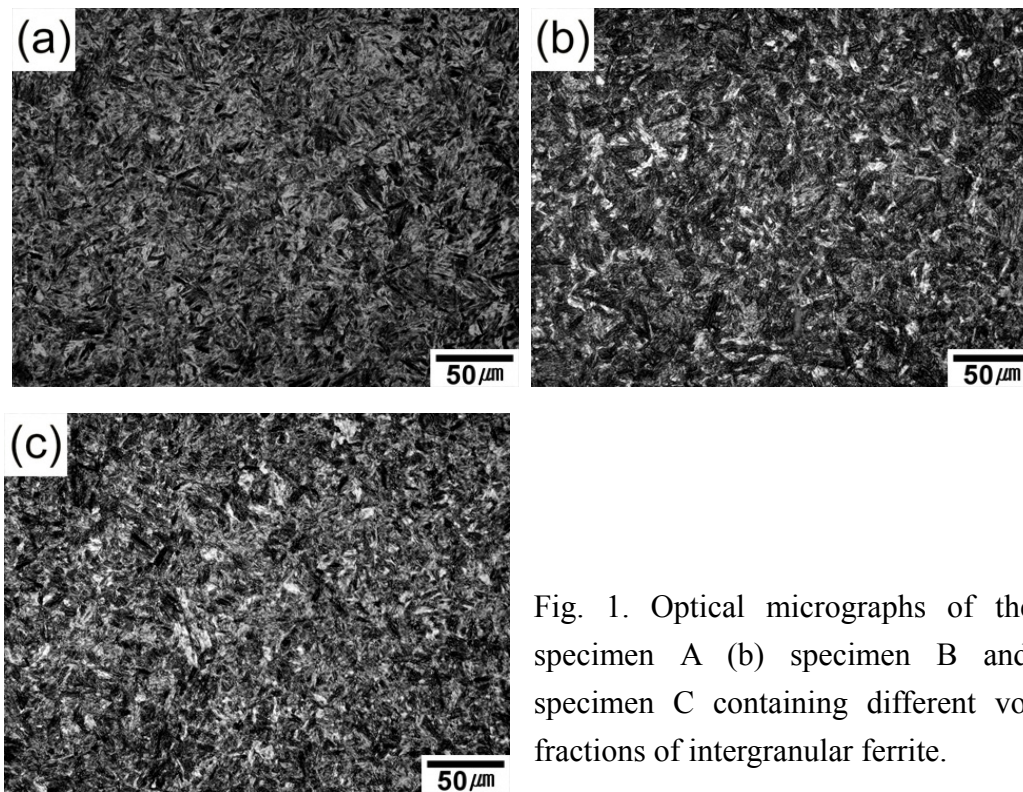


Fig. 1. Optical micrographs of the (a) specimen A (b) specimen B and (c) specimen C containing different volume fractions of intergranular ferrite.

The specimen A exhibited a fully tempered martensite structure and specimens B and C revealed tempered martensite and intergranular ferrite with small volume fractions. The ferrites would be formed first at prior austenite grain boundaries when the specimens cooled down from austenitizing temperature. So, it is thought that the intergranular ferrites were formed at prior austenite grain boundaries because all three specimens were hold for 5 minutes above the austenitizing temperature, i.e., 870°C. The steels showed a relatively uniform distribution of prior austenite grain size, with a mean size of 21 μm , indicating no abnormal growth of austenite grain during austenitization.

The results of constant loading tests with pre-charged specimens are shown in Fig. 2. It is noted that specimen A fractured at the earliest time among three specimens, especially at high stress ratios (0.8 and 0.9). It is clearly evidenced that the time to failure became prolonged with the increase of intergranular ferrite volume fractions.

Typical TDA curves of the steel are shown in Fig. 3. At the heating rate of 300K/h, all of the specimens showed a hydrogen desorption peak at a temperature about 400K. The hydrogen contents corresponding to the peaks were 1.4×10^{15} H atoms, 7×10^{15} H atoms, and 7.8×10^{15} H atoms for A, B and C specimens, respectively. On the basis of the shift

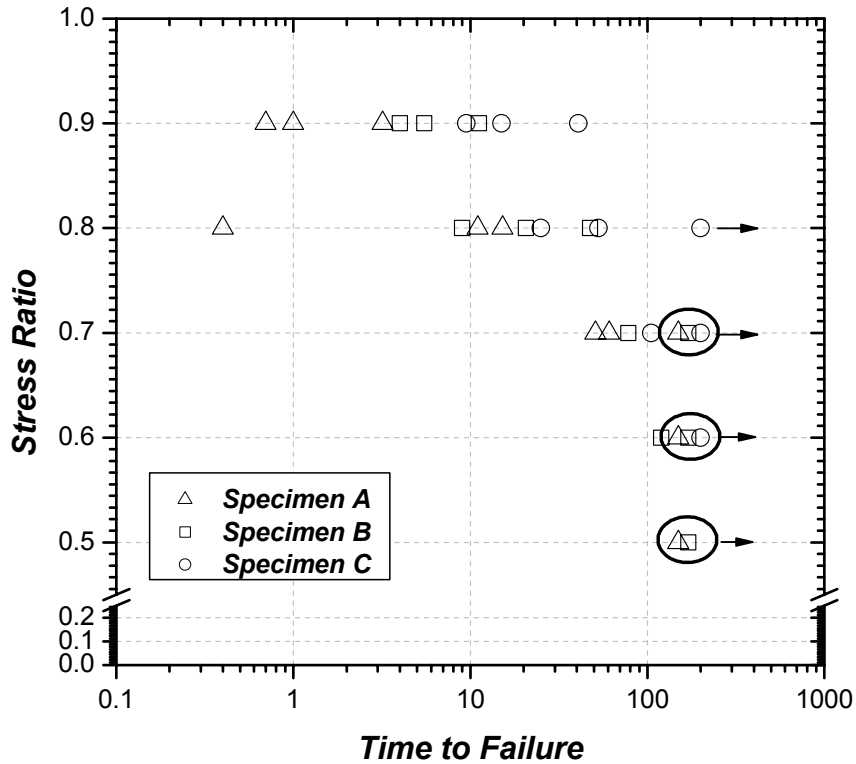


Fig. 2. Stress ratio vs time-to-failure plot obtained from the constant loading test.

of the peak temperature with heating rate, as proposed by Kissinger[8], the activation energy values of hydrogen desorption were calculated to be 16 kJ/mol, 21 kJ/mol and 19 kJ/mol for A, B and C specimens, respectively. It is believed that hydrogen is likely to be trapped by structural defects such as grain boundaries, dislocations, carbides, and micro-voids due to its extremely low solubility in the iron lattice [9-12]. The hydrogen trapping effect depends on the trapping site type and the activation energy of hydrogen desorption reveals the type of trapping sites. The activation energy values of hydrogen desorption for grain boundaries, dislocations, and micro-voids were reported, by Choo and Lee, to be 17.2, 26.8 and 35.3 kJ/mol at the peak temperatures of 385, 488, 578 K, respectively [3]. Considering the result of the earlier work, it is likely that the temperature peak observed in this study mainly corresponds to the hydrogen trapped by grain boundaries. Also, it is known that the amount of hydrogen trapping is largely dependent on the carbide size and morphology. The coarse and film-like carbides are susceptible to hydrogen degradations and act as a crack initiation site [13]. TEM

observation (Fig. 4) reveals that film-like carbides were formed in specimen A, while the amounts of those were significantly reduced in specimens B and C, indicating that the film-like carbides were reduced with the increase of intergranular ferrite volume fraction.

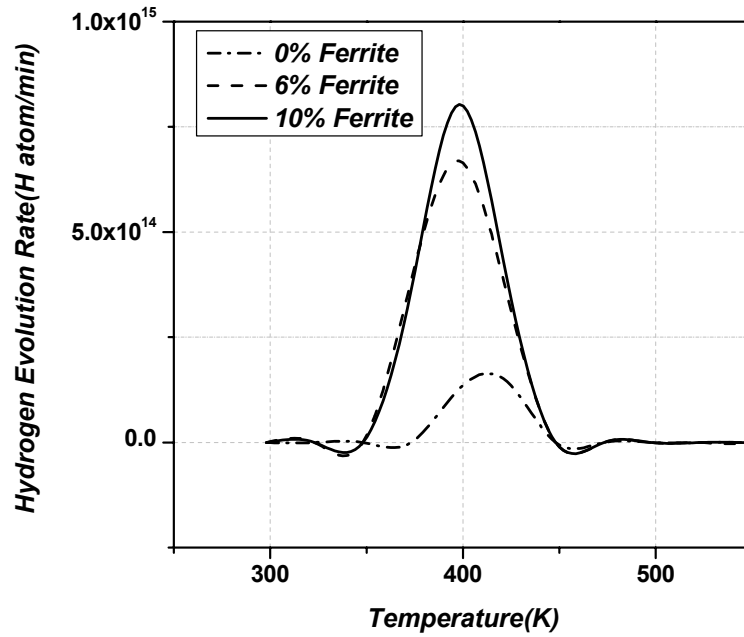


Fig. 3. Hydrogen content – temperature plot obtained from the thermal desorption analysis.

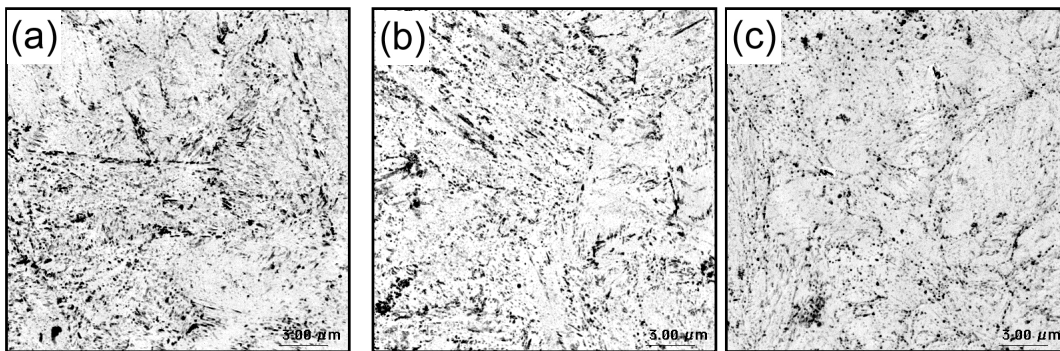


Fig. 4. Transmission electron micrographs (obtained by replica method) of (a) specimen A (b) specimen B and (c) specimen C.

SEM observation revealed that the specimen A exhibited a brittle fracture surface while the specimens B and C showed a ductile fracture surface such as dimples, as shown in Fig. 5, implying that the introduction of intergranular ferrite in the specimen caused a ductile fracture. If the cracks propagating along the grain boundaries met a soft phase, i.e., intergranular ferrite, the propagation would be retarded. This observation was consistent with the results in Fig. 2. As revealed by SEM images (Fig. 6), the intergranular ferrites formed at prior austenite grain boundaries obstruct the propagation of cracks caused by hydrogen. Also, the crack length and volume fraction of cracks were decreased with the increase of intergranular volume fraction. In Fig. 6, the mean crack length was measured in the specimens A, B and C to be 3.8, 2.3 and 1.4 μm , respectively. The volume fraction of cracks was also measured in the specimens A, B and C to be 12.3%, 5.7% and 3.4%, respectively.

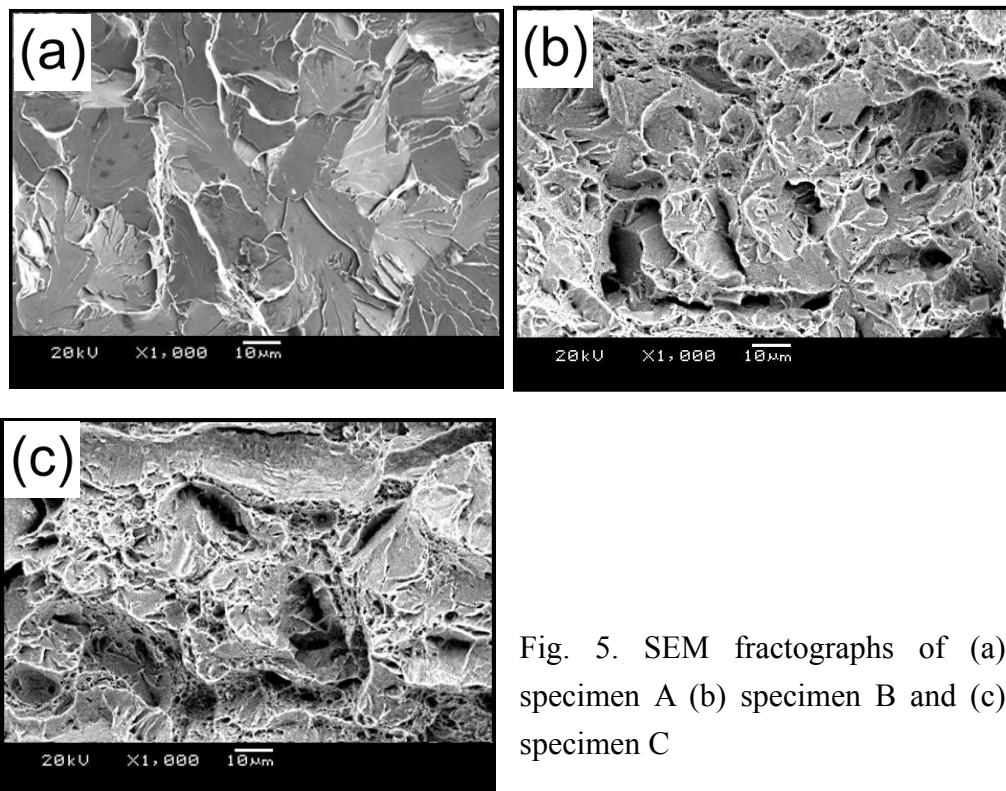


Fig. 5. SEM fractographs of (a) specimen A (b) specimen B and (c) specimen C

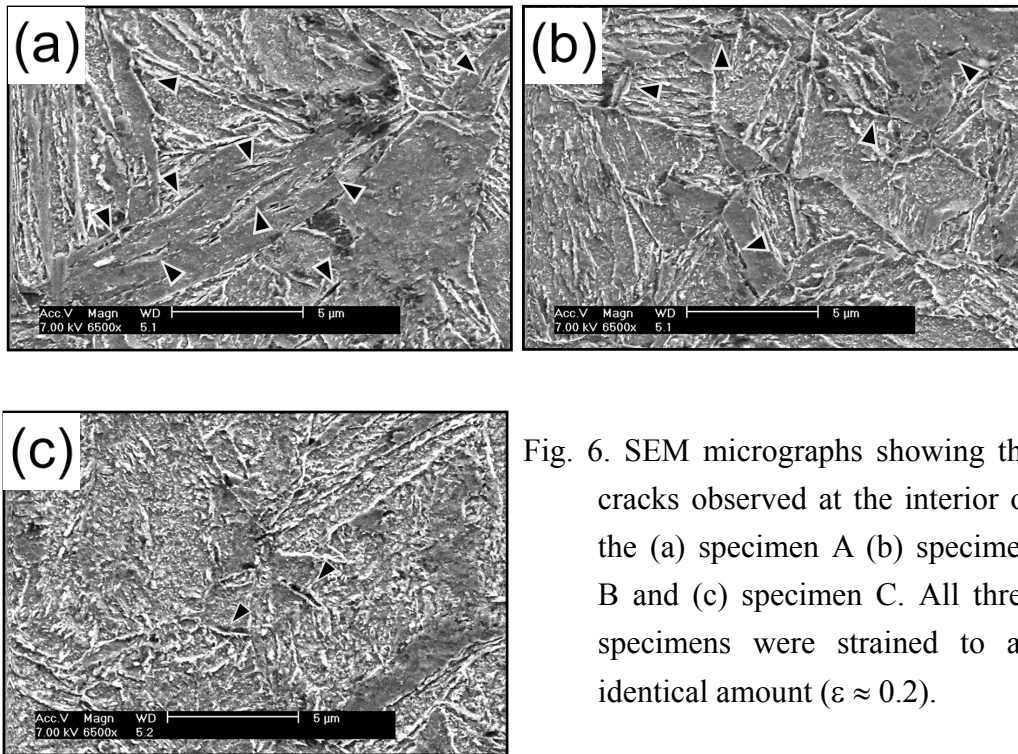


Fig. 6. SEM micrographs showing the cracks observed at the interior of the (a) specimen A (b) specimen B and (c) specimen C. All three specimens were strained to an identical amount ($\epsilon \approx 0.2$).

According to the present TDA analysis and earlier works, most of the hydrogen emitted at low temperatures ($350^{\circ}\text{C}\sim 450^{\circ}\text{C}$) was considered the one trapped by the grain boundaries. With the increase of intergranular ferrite volume fractions, the amount of hydrogen trapped in the grain boundaries increased and the fracture life became prolonged. It is usually suggested that the more the hydrogen content in the steel, the shorter the failure life [14]. However, our TDA analysis (Fig. 2) shows the reverse trend. Here, it is important to consider another factor named as “the critical hydrogen content” which is sufficient to cause the crack initiation. If the diffusible hydrogen content does not reach the critical hydrogen content, then failure will not occur. In this study, by the introduction of intergranular ferrite, total grain boundary area was increased, which would act as a hydrogen trapping site. Accordingly, the critical hydrogen content would be increased. When measuring the critical hydrogen content of the specimens A, B and C, they were found to be 1.4 ppm, 2.8 ppm and 3.3 ppm, respectively. Therefore, in assessing the ability of delayed fracture resistance of a material, two factors are important to consider; one is the amount of diffusible hydrogen and the other is the critical hydrogen content.

4. CONCLUSIONS

Hydrogen delayed fracture resistance of a boron-added steel at the tensile strength level of 1100 MPa was improved by the introduction of intergranular ferrite. Time to failure of the constant loading test for hydrogen charged specimen became prolonged with the increase of intergranular ferrite volume fraction. The intergranular ferrite acts as a barrier to propagation of cracks along prior austenite grain boundaries and as an obstruction against formation of film-like carbides at grain boundaries. From the TDA analysis and earlier works, it was presumed that the pre-charged diffusible hydrogen was trapped mostly by grain boundaries. The critical hydrogen content for crack initiation was found to increase with increasing intergranular ferrite.

ACKNOWLEDGEMENT

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