The effect of pearlite on the hydrogen-induced ductility loss in ductile cast irons

T Matsuo$^{1,2}$

$^1$Department of Mechanical Engineering, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka, 814-0180, Japan
$^2$Institute of Material Science and Technology, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka, 814-0180, Japan

E-mail: tmatsuo@fukuoka-u.ac.jp

Abstract. Hydrogen energy systems, such as a hydrogen fuel cell vehicle and a hydrogen station, are rapidly developing to solve global environmental problems and resource problems. The available structural materials used for hydrogen equipments have been limited to only a few relatively expensive metallic materials that are tolerant for hydrogen embrittlement. Therefore, for the realization of a hydrogen society, it is important to expand the range of materials available for hydrogen equipment and thereby to enable the use of inexpensive common materials. Therefore, ductile cast iron was, in this study, focused as a structural material that could contribute to cost reduction of hydrogen equipment, because it is a low-cost material having good mechanical property comparable to carbon steels in addition to good castability and machinability. The strength and ductility of common ductile cast irons with a ferritic-pearlitic matrix can be controlled by the volume fraction of pearlitic phase. In the case of carbon steels, the susceptibility to hydrogen embrittlement increases with increase in the pearlite fraction. Toward the development of ferritic-pearlitic ductile cast iron with reasonable strength for hydrogen equipment, it is necessary to figure out the effect of pearlite on the hydrogen embrittlement of this cast iron. In this study, the tensile tests were conducted using hydrogen-precharged specimens of three kinds of ferritic-pearlitic ductile cast irons, JIS-FCD400, JIS-FCD450 and JIS-FCD700. Based on the results, the role of pearlite in characterizing the hydrogen embrittlement of ductile cast iron was discussed.

1. Introduction
A new energy network utilizing hydrogen has been developed as a solution for increasing global warming and energy resource problems. Although a lot of efforts are undertaken for a development of hydrogen energy equipments such as a fuel cell vehicle and a hydrogen station, there are still many obstacles to overcome. From the viewpoint of material strength, hydrogen embrittlement (i.e. the degradation of strength properties due to hydrogen penetration into a metallic material) needs to be solved to ensure the integrity of hydrogen energy society. At present, to address this problem, only a few relatively expensive metallic materials which are less susceptible to hydrogen embrittlement (e.g. austenitic stainless steel containing high Ni content) are used for hydrogen equipments in Japan [1].
This is a reason why such hydrogen equipments involve a significant cost. Toward the realization of a hydrogen energy society, it is essential to expand the range of materials available for hydrogen equipments to include inexpensive, common materials. Therefore, ductile cast iron (DCI) was focused in this study as a candidate of low cost, common material available for hydrogen equipments.

DCI is characterized by good mechanical properties (strength, toughness and wear resistance) and therefore, it is used for a variety of applications such as a crankshaft and a gear in cars and pipeline, etc. One noticeable advantage of casting manufacturing is its geometric freedom for product design. In other words, casting manufacturing offers an inexpensive, easy production of monolithic structural components of complex geometry. Therefore, the high production cost for an intricately shaped component and multiple part assemblies is expected to be reduced by shift from conventional steel-based fabrication technique (e.g. machining, mechanical joint and weld) to DCI-based one. If the resistant design to hydrogen embrittlement for DCI is established, casting can be a new option for manufacturing the hydrogen equipments, which will contribute to a cost reduction.

A wide range of mechanical properties of DCIs mainly depends on the matrix structure (e.g. ferrite, pearlite, ferrite-pearlite, martensite and austenite) obtained by the control of chemical composition and heat treatment. In commonly used ferritic-pearlitic DCIs, the strength and toughness are controlled by the volume fraction of pearlitic phase. Regarding carbon steels, it has been reported that a pearlitic phase is susceptible to hydrogen embrittlement [2-4]. Nishiguchi et al. [2] investigated the effect of hydrogen and pearlite on the tensile properties of several kinds of carbon steels, and reported that the ductility loss due to hydrogen was pronounced with increase in the volume fraction of pearlitic phase. Accordingly, it is important to elucidate the pearlite effect on the hydrogen embrittlement of common ferritic-pearlitic DCIs as well. However, there are only a few researches [5, 6] on the hydrogen embrittlement of DCIs and the effect of pearlite has not been reported.

In this study, the tensile tests were carried out using hydrogen-precharged specimens of three kinds of ferritic-pearlitic DCIs: JIS-FCD400, JIS-FCD450 and JIS-FCD700. The effect of pearlite on hydrogen-induced ductility loss was investigated in terms of strain rate dependency.

2. Experimental procedure

2.1. Material and specimen

Three kinds of ferritic-pearlitic DCIs with different volume fraction of pearlite were used in this study: JIS-FCD400 with an almost fully ferritic matrix, JIS-FCD450 with a ferritic matrix with sparsely distributed pearlitic phase and JIS-FCD700 with a pearlitic matrix containing a thin ferritic envelope surrounding graphite. Microstructures of these DCIs are shown in Fig. 1. The chemical compositions are listed in Table 1. The tensile specimen shown in Fig. 2 was machined from as-cast blocks and then polished by a #2000 emery paper and paste of alumina particles with a diameter of 1 µm.

![Microstructures](image-url)
2.2 Hydrogen charging and tensile test
In order to charge hydrogen in a specimen, the specimen was soaked in a 20 mass% of aqueous solution of NH₄SCN at 40 °C prior to tensile test. The hydrogen charging times were 24 h for FCD450 and 168 h for FCD400 and FCD700. These specimens were hereafter called 24h-charged specimen and 168h-charged specimen, respectively, whereas the specimen without hydrogen charging was called uncharged specimen.

The tensile tests for both of charged and uncharged specimens were conducted in air at ambient temperature. To elucidate the strain rate dependency on hydrogen-induced ductility loss, the tests were conducted at different cross head speeds (CHS) of 0.02 mm/min, 1 mm/min (only for FCD450) and 50 mm/min.

2.3 Analysis of hydrogen storage and fracture morphology
The amount of hydrogen adsorption into a specimen after hydrogen charging was measured by a thermal desorption spectroscopy (TDS) in which temperature was raised up to 800 °C at a rate of 0.5 °C/sec.

Fracture surface was observed by a scanning electron microscope (SEM). The fracture morphology inside the material, e.g. void growth and coalescence and crack initiation, was examined by observing the longitudinal cross section of tensile-fractured specimen.

3. Results and discussion

3.1 Hydrogen content
The hydrogen contents of hydrogen-charged specimens obtained by TDS measurement are listed in Table 2 together with the mean graphite diameters and the area fractions of ferrite, pearlite and graphite. Regardless of area fraction of pearlite, a much greater amount of hydrogen was stored in DCI than in ordinary carbon steel. In general, the amount of hydrogen storage of hydrogen-charged carbon steel is less than or comparable to 1 mass ppm [7]. Takai et al. [8] reported that most of hydrogen in hydrogen-charged ferritic-pearlitic DCI exists in the graphite-matrix interface. Ogi et al. [9] also reported the similar results for ferritic DCI. Matsunaga et al. [5] figured out that a large amount of hydrogen was stored not only at the graphite-matrix interface but also inside the graphite nodule by using the hydrogen microprint technique. The hydrogen content of DCI was much larger compared with the increase in hydrogen content of carbon steel when the fraction of pearlitic phase was increased [2]. Therefore, it is concluded that the graphite-matrix interface and the inside of graphite nodule are a major hydrogen storage site for ferritic-pearlitic DCI.

---

Table 1. Chemical compositions.

|       | C   | Si  | Mn  | P   | S   | Cu  | Mg  |
|-------|-----|-----|-----|-----|-----|-----|-----|
| FCD400| 3.68| 2.16| 0.29| 0.024| 0.010| 0.01| 0.035|
| FCD450| 3.70| 1.78| 0.34| 0.058| 0.007| -   | -   |
| FCD700| 3.77| 2.99| 0.44| 0.023| 0.110| -   | -   |
3.2 Relationship between ductility loss and crosshead speed (CHS)

Figure 3 shows the stress-strain curves obtained by the tensile tests of FCD400 and FCD700. The strength properties (i.e. flow stress and ultimate tensile stress) were slightly affected by hydrogen, but its effect was not remarkable. On the other hand, the ductility was severely deteriorated by hydrogen. The relative reduction of area (RRA), i.e. the ratio of reduction of area of hydrogen-charged specimen to that of uncharged specimen, is often employed as a measure of the degree of hydrogen embrittlement [10-12]. The RRAs were plotted as a function of CHS in Fig.4. It should be noted that the effect of CHS on the RRA depends on the fraction of pearlite. In FCD450 and FCD700 that contain a certain amount of pearlite, the RRA decreased with decrease in CHS. Namely, decreasing CHS intensified the hydrogen effect on the ductility. This phenomenon is understandable and is consistent with a conventional remark that low strain rate causes a more pronounced degradation owing to increased hydrogen accumulation at the fracture site. In ferritic DCI (FCD400), however, the RRA remained the almost same level despite a decrease in CHS.

**Table 2. Mean graphite diameter, area fraction of each phase and hydrogen content.**

| Material | Mean graphite diameter (μm) | Area fraction (%) | Hydrogen content (mass ppm) |
|----------|-----------------------------|------------------|-----------------------------|
|          |                             | Ferrite | Pearlite | Graphite |                        |
| FCD400   | 38                          | 86      | 2       | 12       | 28.1                     |
| FCD450   | 19                          | 72      | 15      | 13       | 4.4                      |
| FCD700   | 28                          | 22      | 64      | 14       | 7.0                      |

**Figure 3.** Stress-strain curves of FCD400 and FCD700.

**Figure 4.** Relationship between RRA and CHS.
3.3 Fracture morphology

Figure 5 and 6 shows the fracture surfaces of uncharged and 168h-charged FCD400 and FCD700 that are tensile-fractured at CHS of 0.02 mm/min. Regarding FCD400, the fracture surface was covered by dimples originated from graphite nodules in uncharged specimen, whereas the quasi-cleavage fracture was observed partially in 168h-charged specimen. On the other hand, in FCD700, there is no significant difference in between the fracture surfaces of uncharged and 168h-charged specimens. Both of them were mostly covered by brittle-like fracture surfaces and flat fracture surfaces were observed around graphite nodules (see Fig. 6(c)).

Figure 5. Fracture surfaces of FCD400 at CHS = 0.02 mm/min.

Figure 6. Fracture surfaces of FCD700 at CHS = 0.02 mm/min.
Figure 7. Fracture morphologies observed on the longitudinal cross sections of FCD400.

(a) Uncharged, $CHS = 0.02$ mm/min  
(b) Uncharged, $CHS = 50$ mm/min  
(c) 168h-charged, $CHS = 0.02$ mm/min  
(d) 168h-charged, $CHS = 50$ mm/min

Figure 8. Fracture morphologies observed on the longitudinal cross sections of FCD700.

(a) Uncharged, $CHS = 0.02$ mm/min  
(b) Uncharged, $CHS = 50$ mm/min  
(c) 168h-charged, $CHS = 0.02$ mm/min  
(d) 168h-charged, $CHS = 50$ mm/min
In order to elucidate the fracture process under each condition, the longitudinal cross section of the specimen after tensile rupture were observed and the typical images of SEM observation are shown in Figs. 7 and 8. In uncharged FCD400, voids originated from graphite nodules were elongated in the loading direction and then they coalesced to each other (see Fig. 7 (a), (b)). In 168h-charged FCD400, several cracks emanated from some of graphite nodules and grew perpendicular to the loading direction (indicated by arrows in Fig. 7 (c), (d)). These cracks resulted in the quasi-cleavage fracture observed on the fracture surface, which was considered to be a cause of ductility loss in FCD400. On the other hand, in both of uncharged and 168h-charged FCD700, several cracks were observed at the pearlite (see Fig. 8). The brittle-like fracture on the most of fracture surface of FCD700 was attributed to this pearlite cracking. Moreover, the flat fracture around graphite nodules is thought to be due to cracking of the ferrite layer surrounding graphite nodules.

3.4 Effect of pearlite and CHS on the fracture mechanism

Based on the observation of fracture morphology, the fracture mechanism of each condition is considered as schematically shown in Fig. 9. In FCD400 with a fully ferritic matrix, a graphite-matrix debonding is the prologue of fracture [13]. As mentioned above, a great amount of hydrogen exists at the graphite-matrix interface and the inside of graphite nodules. This graphite-supplied hydrogen (at least hydrogen trapped at the interface) fills immediately the interspace between graphite and matrix after debonding [5]. It is well known that hydrogen enhances a localized slip deformation called Hydrogen Enhanced Localized Plasticity, HELP [14, 15], which causes the quasi-cleavage cracking instead of the ductile dimple development. Accordingly, hydrogen supplied from the interspace to crack tip affects the fracture process, resulting in the growth of quasi-cleavage cracking in FCD400. It should be noted that the interspace is filled with hydrogen after debonding, and thereby, the sufficient amount of hydrogen can be supplied to the fracture site even at high CHS (i.e. 50 mm/min). At low CHS (i.e. 0.02 mm/min), although a small amount of hydrogen from the matrix diffuses to the crack

![Figure 9](image-url)
tip, the effect of this hydrogen is very small compared with the hydrogen supplied directly from the interspace. In the case of FCD400, as a consequence, the hydrogen-induced ductility loss was not affected by CHS.

In FCD700, the pearlite cracking occurs in both uncharged and 168h-charged specimens. It has been reported that the growth of pearlite cracking in carbon steel is facilitated by the accumulation of solute hydrogen at the crack tip [2]. Therefore, the cracking initiated inside the pearlite is facilitated with decrease in the CHS, because the hydrogen supplied from the matrix becomes pronounced owing to the longer loading time. However, the cracking activated by the graphite-matrix debonding is not affected by the CHS in common with the case of FCD400.

In summary, only hydrogen that is supplied from graphite nodules plays a key role for cracking and thereby degrading ductility in the case of high CHS. In addition to this mechanism, in the case of low CHS, the hydrogen accumulated at the crack tip via the matrix is also influential for cracking inside the pearlite in FCD700 and as a result, assists the extension of fracture surface, reducing ductility. This is probably the reason why the hydrogen-induced ductility loss of ferritic-pearlitic DCIs becomes more susceptible to CHS with increase in the volume fraction of pearlite.

4. Conclusions

The tensile tests of hydrogen-charged ferritic-pearlitic DCIs with different volume fraction of pearlite were conducted. The effect of pearlite on the hydrogen-induced ductility loss of DCI was investigated in terms of strain rate dependency and the following conclusions were obtained:

1. The amount of hydrogen stored in ferritic-pearlitic DCI was much greater than that in ordinary carbon steel and it poorly correlated with the volume fraction of pearlite.
2. In FCD450 and FCD700 that contain a certain amount of pearlite, the reduction of area (RRA) decreased as the crosshead speed (CHS) decreased and this tendency was more pronounced in FCD700 than in FCD450. In FCD400, on the other hand, the RRA remained almost the same level despite a decrease in CHS.
3. In FCD400, the void growth and coalescence were mainly observed for the fracture process of uncharged material, while the quasi-cleavage cracking occurred partially in hydrogen-charged material. In FCD700, regardless of hydrogen-charging, pearlite cracking accounted for the majority of fracture process.
4. The difference in strain rate dependency of hydrogen-induced ductility loss in between ferritic-pearlitic DCIs can be explained as follows. At high CHS, only hydrogen that is supplied directly from interspace due to the graphite-matrix debonding plays a key role for degradation of ductility. At low CHS, additionally, the small amount of hydrogen supplied from the matrix accumulates at the crack tip. This hydrogen accumulation can not work for cracking from graphite nodule in FCD400 because a large amount of hydrogen inside the crack affects its growth dominantly, resulting in no strain rate dependency. On the other hand, in FCD700, the hydrogen supply from the matrix assists cracking inside the pearlite together with cracking from graphite that is facilitated by hydrogen supplied from graphite itself, and consequently it contributes further degradation of ductility with decrease in CHS.

Acknowledgment

The author would like to thank Mr. T. Usuda for his extensive experimental works.

References

[1] Yamada T and Kobayashi H 2012 Koatsu gas 49 885-93
[2] Nishiguchi H, Fukushima Y, Matsuoka S and Murakami Y 2008 Trans. Jpn. Soc. Mech. Eng. A 74 1016-25
[3] Nishiguchi H, Fukushima Y, Matsuoka S and Murakami Y 2010 Trans. Jpn. Soc. Mech. Eng. A 76 1459-68
[4] Costa J E and Thompson A W 1982 Metall. Trans. A 13 1315-18
[5] Matsunaga H, Usuda T, Yanase K and Endo M 2014 Metall. Mater. Trans. A 45 1315-26
[6] Matsunaga H, Nakashima T, Yamada K, Matsuo T, Yamabe J and Matsuoka S 2016 ASME. Pressure Vessels and Piping Conference 6B PVP2016-63536
[7] Matsuo T, Homma N, Matsuoka S and Murakami Y 2008 Trans. Jpn. Soc. Mech. Eng. A 74 1164-73
[8] Takai K, Chiba Y, Noguchi K and Nozue A 2002 Metall. Mater. Trans. A 33 2659–65
[9] Ogi K, Hagi H, Tahara A, Sawamoto A, Ikeda H and Hayashi Y 1992 J. Jpn. Found. Eng. Soc. 64 186–91
[10] Safety Standard for Hydrogen and Hydrogen Systems 2005 NASA NSS 1740
[11] Michler T and Naumann J 2010 Int. J. Hydrogen 35 821-32
[12] San Marchi T, Michler T, Nibur K A and Somerday B P 2010 Int. J. Hydrogen 35 9736-45
[13] Dong M J, Prioul C and François D 1997 Metall. Mater. Trans. A 28 2245-54
[14] Beachem C D 1972 Metall. Trans. 3 437-51
[15] Birnbaum H K and Sofronis P 1994 Mater. Sci. Eng. A 176 191-202