

Hydrogen Degradation of High Strength Steel Weldments

by

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Submitted to the Department of Ocean Engineering and the Department of Materials Science and Engineering on May 18, 1993, in partial fulfillment of the requirements for the degrees of Engineer's in Ocean Engineering and Master of Science in Material Engineering

Abstract

The phenomenon of hydrogen assisted cracking is well known as far as the weldments of low strength steel are concerned. Recently, during the arc welding of high strength steels, a large number of small cracks in the weld metal has been observed, contrary to what it has been observed during the welding of low strength steels i.e., a small number of larger cracks in the HAZ.

In this study, it is hypothesized that the fine dispersion of inclusions present in the weld metal of high strength steels is responsible for the observed differences in cracking. This hypothesis was found to be well supported by the following facts: (a) the fine dispersion of inclusions is able to trap a relatively large amount of hydrogen, (b) the hydrogen has the tendency to migrate towards regions under high triaxial tensile stress i.e., the crack tip plastic zones, (c) once the crack tip advances out of the former plastic zone-into a region in which the hydrogen concentration is less than the critical value-the crack is arrested. Because of the large variation of the diffusion coefficient at room temperature, it will take too long for a crack to grow even to a length of approximately one centimeter. Furthermore, the remaining hydrogen moves towards crack nucleation sites, which are nearer, causing the formation and limited growth of new cracks, instead of moving towards a specific crack tip-and thus raise the crack growth rate.

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Introduction

In the marine industry, the need to build more efficient and more cost effective structures, dictates the need to develop high strength steels, with high strength-to-weight ratio. This is especially true in submersible applications, where the development of high strength tempered steels has brought with it many problems of joining by arc welding. In construction of submersibles where these high strength to weight ratio steels are most commonly used, strict safety standards cause rejection of structural members for otherwise relatively minor flaws. Consequently, the cost of the structure increases dramatically¹.

Weld hydrogen embrittlement refers to loss of ductility of the material, which results in cracking or failure, usually soon after the weld is completed. Nevertheless, hydrogen cracking can occur later in service under unusual conditions. In one case the hydrogen concentration was found to be 1 cc/100 gram in a mild steel weldment, ten years after the welding process took place [9].

This form of cracking is also called cold cracking, delayed cracking or hydrogen assisted cracking. The hazardous behavior of hydrogen, is a complex phenomenon which includes the amount of hydrogen, the applied stress, the temperature and the microstructure involved. In the past, many studies have been performed, investigating and trying to model the effect of hydrogen on the properties of steel².

The fact that cracking may occur after a relatively long time (days or weeks after fabrication), causes great concern over the integrity of the structures. In

¹In Britain alone, the estimated annual cost of repairing the structures affected by hydrogen embrittlement, amounts to over one hundred and forty million pounds [28].

²See bibliography.

particular, it has been observed that when welding steels with yield points over 690 MPa -(100 ksi), a large population of small cracks in the weld metal is observed whereas when welding lower strength steel, a small number of longer cracks in the heat affected zone (HAZ) is observed. Since the cause of this different cracking behavior is not known, the purpose of the present study is to investigate, using analytical means, the role of large population of inclusions in the weldment, as far as the solubility and diffusion of the hydrogen are concerned. It is hypothesized the presence of a fine dispersion of inclusions may be able to explain the observed differences in hydrogen cracking behavior between low strength and high strength steel weldments.

Chapter 1

Background

1.0.1 Sources of Hydrogen during Welding and Hydrogen Absorption

The typical causes of hydrogen entrance and theories that govern the saturation and solubility of hydrogen in ferrous weld metals can be found in [11, p. 28] and [30]. The amount of hydrogen that exists in fluxes for various types of electrodes and welding methods, as well as the fraction of that amount that finally enters the weld metal can be found in [5]. Theories that explain the mechanism of the above phenomenon are described in [11, p. 27].

1.0.2 Hydrogen Diffusion

The hydrogen diffusion is governed by the Fick's first and second law [6]. The driving forces for diffusion are described in [11, p. 36].

1.0.3 Trapping of Hydrogen

The diffusivity of hydrogen in iron, especially below $250^{\circ}C$, is greatly affected by the presence of traps. The effect of trapping on hydrogen diffusion has been extensively researched, to determine the density, depth, and interaction energies of the various trapping sites such as microvoids, grain boundaries, inclusions, microcracks, solute

elements and other structural non-uniformities [19, 22, 9, 42, 21, 36, 18]. These imperfections have an affinity for the hydrogen which results in a binding energy of the hydrogen to the defect. The binding energy is a measure of the trapping strength of hydrogen and determines the effectiveness of a trap. Available data [17] suggest that dislocations and grain boundaries are equally effective, while the interfaces of internal microvoids, nitrides and carbides have larger binding energies. That means that when a hydrogen atmosphere is dragged along by a moving dislocation¹ and when that dislocation passes by such interfaces, the relative chemical potentials are such that hydrogen will strongly tend to accumulate at that interface. Such atmospheres can be dragged by dislocations large distances, $\sim 1mm$, in an otherwise perfect crystal. Tien [42] reports that in iron-base alloys after a deformation time of sixty seconds, \sqrt{Dt} diffusion penetration is of the order of microns while hydrogen transport due to dislocation motion (sweeping), is of the order of centimeters.

In a special case, when the inclusion is a microvoid [42] or the void is a part of an inclusion, the hydrogen seeps into the void, recombines to the diatomic form and thus balances thermodynamically the local fugacity inside the void. That void will be continuously charged or pressurized with hydrogen if the arrival rate by the dislocation transport mechanism is faster than the rate of hydrogen diffusion into the surrounding matrix. Such a pressure build up, may later contribute to embrittlement, by enhancing the crack growth or dimple growth. Leakage from the void may prevent significant pressurization; however, when hydrogen adsorption poisons, like oxygen, segregate to the interface² such leakage does not occur.

1.0.4 Crack and Crack-Propagation

A critical combination of stress state and hydrogen concentration is needed to initiate cracking. In other words, crack nucleation occurs because of the reduction in cohesive strength of the metal lattice, or when the hydrogen content in the area of

¹The dislocation has to move with velocity less than a critical value which is a function of temperature and strain rate, in order to drag the hydrogen atmosphere along [38, p. 284].

²That can happen either through rejection by the matrix or by the inclusions.

maximum triaxial stress reaches a critical value as a result of stress induced hydrogen diffusion in that region. Once the crack initiates, it propagates until arrested in a region of lower hydrogen content. Further diffusion of hydrogen to the new region where the triaxial stress is maximum will re-initiate crack propagation, see fig: 1-1.

From a fracture mechanics point of view, hydrogen assisted cracking, can occur at stress intensity factors³ less than 25% of the fracture toughness⁴[32] of the material. For high strength steels in which the $K_{I_{sc}}$ ⁵ drops as the yield stress increases, see fig: 1-2, crack initiation and propagation are very sensitive to hydrogen concentration i.e., only a small amount of hydrogen is needed to initiate or re-initiate crack propagation.

A small crack of a fixed size is more likely to start hydrogen-cracking in residual⁶ stress fields of a high strength, than a low strength, material since:

- the yield stress is higher and the stress intensity factor K is higher
- higher strength material has lower resistance to environmental cracks.

It has been also noted [37, p. 983], that after the magnitude of the strength-intensity factor is increased by applying more stress to a WOL⁷ specimen that has a static crack, the hydrogen pressure required to just propagate the crack is essentially the same as that at which the crack comes to a stop at the same value of K. However, if instead of applying a monotonically increasing load, the same value of K is attained by unloading from a larger value of K, it is usually found that higher hydrogen pressure is needed to propagate the crack. That is called *The hysteresis phenomenon*[37].

³Stress intensity factor is defined as $K = \beta\sigma\sqrt{\alpha}$, where σ is the applied stress, β is a dimensionless parameter depending on the geometry of the cracked body and α is the half-length of the crack.

⁴The stress intensity factor associated with the stress that causes fracture is called fracture toughness.

⁵The stress intensity factor below of which stress corrosion cracking does not occur.

⁶Case applied to weldments.

⁷This test has the characteristic that as the crack propagates, the stress intensity factor drops constantly; it is used if self-arrest of the crack under constant pressure of hydrogen gas needs to be assured. Furthermore, it is easy to control the progress of a crack-see [37, 35].

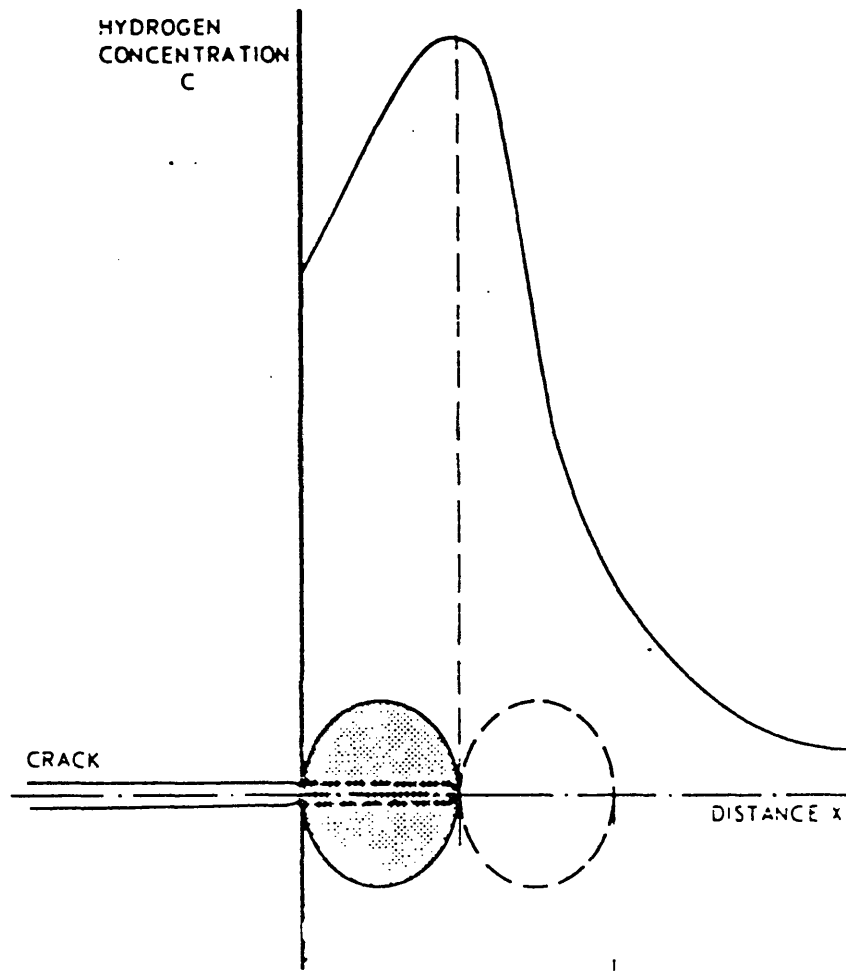


Figure 1-1: Crack propagation and arrest

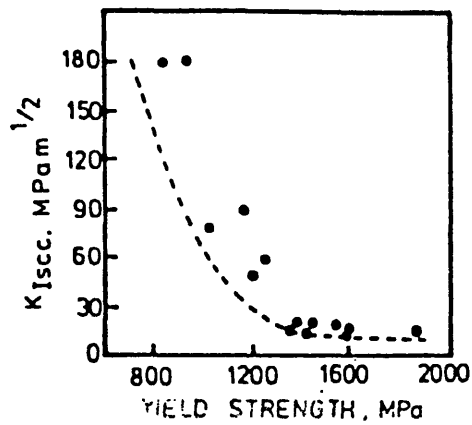


Figure 1-2: Influence of strength level on K_{Isc} for ferritic steels in hydrogen gas pressure of 100-400 kPa

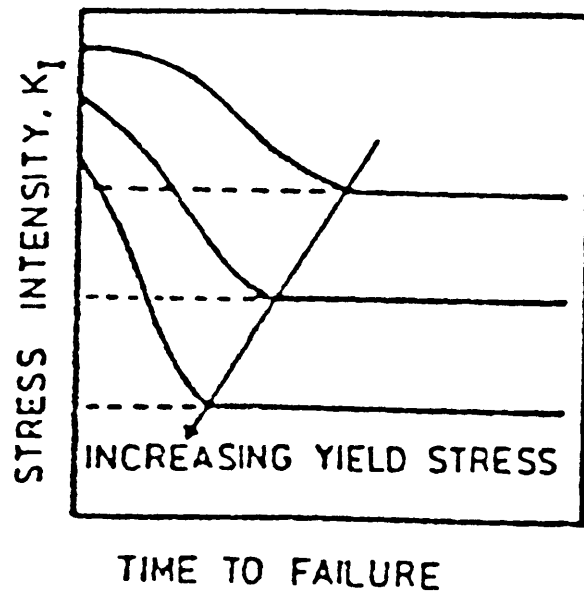


Figure 1-3: Schematic illustration of the effect of strength level on K_{Isc} for hydrogenated steel

Chapter 2

Analytic Investigation

2.1 Inclusions

In this study the role of the inclusions is investigated regarding their effect on cracking of the weld metal. Not too many studies have been done regarding the quantitative analysis of the inclusions in the weld metal of high strength steels. One that was done for HSLA is that of [29], whose results will be used in this study. In that paper [29], various electrodes were used and the population and diameter of the consequent inclusions were measured as shown in table 2.1. The effect of the inclusions on cracking has been hypothesized to be trapping of hydrogen and essentially decreasing the available amount of hydrogen that can migrate towards the crack tip and thus the cracking growth rate is decreased.

This hypothesis came from the simple fact that the dispersion of the finer particles is larger in high strength steel (HSS) than in low strength steel (LSS) weld metals; so, assuming that the volume fraction of inclusions in the above weld metals is the same, since the particle diameter in the weld metal of LSS is larger (approximately two orders in magnitude as shown in appendix D) than that of HSS, the difference in the population of the inclusions is about seven orders of magnitude higher in HSS. Consequently, the adsorbing surface of the inclusions in HSS is larger i.e., the amount of trapped hydrogen is larger. From the well known relationship $x \propto \sqrt{Dt}$, a typical value of diffusion coefficient of hydrogen in steel

<i>various types of welds</i>	<i>inclusion vol. fraction</i>	<i>diameter micrometers</i>	<i>density 10⁸ 1/mm³</i>
S313H	0.33	0.27	7.6
SG13H	0.004	0.51	2.01
EH133H	0.033	0.42	2.99
EM13H	0.0051	0.42	6.4
Ti13H	0.0033	0.4	3.27
TiOeH	0.0025	0.33	1.54

Table 2.1: Summary of inclusion data [29]

$D = 10^{-7} \text{ cm}^2/\text{sec}$ and a large time interval $t = 10^4 \text{ sec}$, the diffusion distance of the already reduced-by the trapping effect-amount of hydrogen yields to $316 \mu\text{m}$. Taking into account that a specific value of hydrogen concentration is necessary—with constant applied stress for the crack to propagate, an extremely large amount of time is needed. Consequently, despite the fact that hydrogen has the tendency to migrate towards the regions under higher triaxial stresses, it will migrate towards a closer crack nucleation site.

At the beginning of this study, one of the issues that was to be answered is how to determine the maximum amount of hydrogen that can be trapped by the inclusions in the weld metal. For that reason, it is assumed that hydrogen is adsorbed on the inclusions, the way that it adsorbs on iron [4], since there is no evidence of how hydrogen adsorbs on the inclusions formed in the weld metal. During the subsequent calculations the following postulates have been made:

1. The shape of the inclusions is spherical.
2. The inclusions are equally spaced in the weld metal.

Since the amount of hydrogen adsorbed on the inclusions is not specifically determined, three cases were examined as follows¹:

¹The calculations of the procedures are shown in appendix A.

1. Assuming that the inclusion structure is BCC and one atom of hydrogen is sitting on each atom of the inclusion being on the close-packed-plane (111), the amount of hydrogen trapped is:

$$M_H = \frac{2.12 \times 10^{15} A}{N_A} \quad (2.1)$$

where M_H is the amount of trapping hydrogen in grams, A is the total area of inclusions in cm^2 and N_A is the Avogadro's number.

2. Knowing the atomic radius of hydrogen (0.79 \AA) and assuming that a specific area of the inclusion particle should be covered with hydrogen atoms located one next to the other, the number of hydrogen atoms can be found by dividing the area of the particle by the area of the projection of the spherical atom on the particle.
3. Using a saturation value for hydrogen adsorbed on the particle, the value given by [20] i.e., $10^{15} \text{ atoms}/cm^2$.

The values² found for each of the above cases are:

1. 0.75 ppm.
2. 1.7 ppm.
3. 0.4 ppm.

respectively.

2.2 The Role of the Plastic Zone at the Crack Tip

The stress distribution³ ahead of the crack tip has the form shown in fig: 2-1. As predicted from continuum mechanics, the maximum stress is approximately $3 \times \sigma_y$

²Using the average particle diameter $d_{cr} = 0.371 \mu m$ and population $N_v = 3.76 \times 10^8 mm^{-3}$ as shown in appendix C.

³Under plane strain conditions.

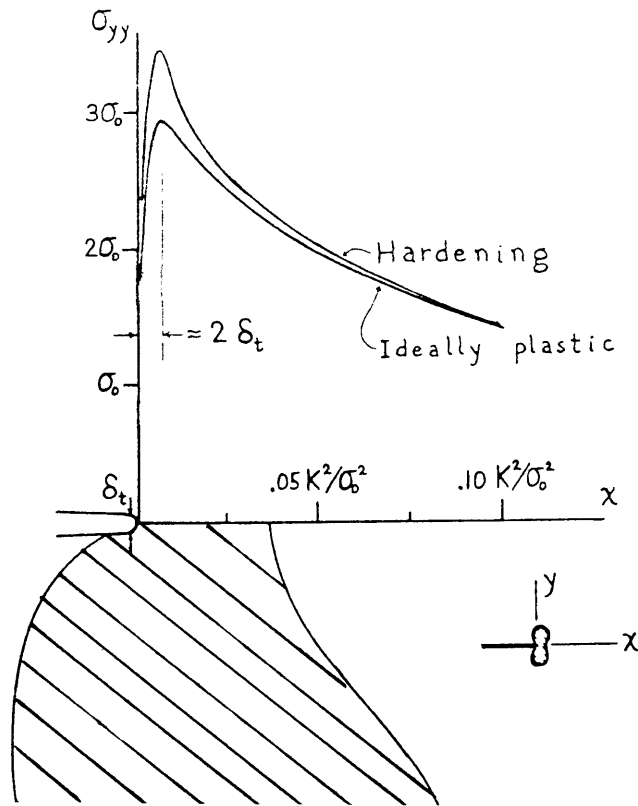


Figure 2-1: Stress Distribution in Front of the Crack Tip

for an ideally plastic solid and even higher when strain hardening is involved [39]. As pointed out by Rice [39], an increase in load⁴ does not change the stress level acting, but simply expands the curves shown over a wider region of material ahead of the crack tip, by K_{Ic}^2/σ_y^2 . Since hydrogen solubility increases with triaxial tensile stress⁵, it can be expected that additional hydrogen is led towards the crack tip. Considering the above, one could conclude that the critical hydrogen concentration is a material property and is independent of the externally applied stress⁶. This is because the stress singularity reduction due to plastic flow, is approximately 3 to $3.5\sigma_y$, independent of stress intensity[14]. The regions where hydrogen is preferably accumulated, depend upon the binding energy of the flaw. Kumnick *et, al* [25, p. 37] suggests that traps are associated with structural imperfections or point defects.

⁴Therefore, an increase in K.

⁵Solubility $\propto e^{10^{-4}\sigma}$, as shown by Rice [39]

⁶Although a minimum stress is required- $K_{I,cc}$.

Therefore, one could expect that crack initiation and propagation mechanisms are triggered by local accumulation of hydrogen at microstructural heterogeneities. Any load increase, broadens the plastic zone of the crack tip and consequently increases⁷ the crack growth rate.

2.2.1 Modeling the Plastic Zone

The hydrogen has a tendency to migrate towards the regions under triaxial stress. For that reason the plastic zone can be assumed to be a hydrogen sink. To simplify the model, it is assumed that the shape of the plastic zone is cylindrical, which can be solved as a two-dimensional disk. The equation⁸—developed by Rideal and Tadayon, which calculates the total amount of diffusing substance Q remaining on a disk of radius a , after time t is as follows.

Defining τ as

$$\tau = \frac{\pi a^2}{2D} \quad (2.3)$$

- For small values of t i.e., $t < \tau$ eq. 2.2 can be written as :

$$Q = \pi a^2 C_o \left(1 - \frac{2}{a} \sqrt{\frac{Dt}{2\pi}}\right)$$

- For large values of t i.e., $t \gg \tau$ the respective equation for eq. 2.2 is :

$$Q = \frac{\pi a^4 C_o}{4Dt}$$

For the case of a disk sink, the above equations can be written as follows:

⁷There is a broader area having higher amount of hydrogen than the critical one-needed to propagate cracking.

⁸The analytic form of the equation[6, p. 28] for a disk-source[6, p. 28] is:

$$Q = 2\pi a^2 C_o \int_0^\infty \frac{J_1^2(ua)e^{-Dtu^2}}{u} du \quad (2.2)$$

where $J_1(ua)$ is the Bessel function of the first kind and of the first order and C_o is the initially uniform concentration in the disk.

$$\bar{C} = C_o \left(1 + \frac{2}{a} \sqrt{\frac{Dt}{2\pi}} \right) \quad (2.4)$$

where \bar{C} is the average concentration after time t and C_o is the initial concentration.

$$\bar{C} = C_o \left(2 - \frac{a^2}{4Dt} \right)$$

for small and large times respectively⁹. It should be pointed out however, that the above equations for disk sink, are valid only for $\bar{C}/C_o < 2$, as shown in appendix B.

The diffusion coefficient, at room temperature, varies [5, p. 52] from 10^{-8} to $10^{-6} \frac{cm^2}{sec}$ and a typical radius of a plastic zone¹⁰, for high strength steel with $K_{Ic} = 64 MPa\sqrt{m}$ and $\sigma_y = 896 MPa$, is $r_p = 8.5 \times 10^{-4} m$. Using the plastic zone radius as disk-sink radius, eq. 2.3 is calculated to be $\tau = 1.1 \times 10^6 sec$ and $\tau = 1.1 \times 10^4 sec$, for the aforementioned diffusion bounds respectively. The value for $t = 10^4 sec$ is a reasonable time for cold cracking. Thus eq. 2.4 will be used for subsequent calculations. In addition, since it has been observed that when cracking occurs, a large number of small cracks having length and spacing among them approximately one centimeter, a control space of $1 cm^2$ is considered. The time needed for the disk-sink hydrogen concentration to reach the critical value—for cracking to occur—is obtained by means of the following equation¹¹:

$$t_{cr} = \frac{2\pi}{D} \left\{ \frac{a}{2} \left(\frac{C_{cr}}{C_o} - 1 \right) \right\}^2 \quad (2.5)$$

⁹Procedure shown in appendix B.

¹⁰By using the equation for plane strain condition:

$$r_p = \frac{1}{2\pi} \left(\frac{K_{Ic}}{\sigma_y} \right)^2$$

¹¹Which yields by solving eq. 2.4 with respect to t .

and differentiating the above equation with respect to C_{cr}/C_o , it yields :

$$\frac{\partial t}{\partial \frac{C_{cr}}{C_o}} = \frac{\pi a^2}{D} \left(\frac{C_{cr}}{C_o} - 1 \right) \quad (2.6)$$

By plotting eq. 2.5 for D in the region of 10^{-8} to 10^{-6} cm^2/sec and t in the region of 10^3 to 10^4 , yields figure 2-2. Figure 2-3 is produced by plotting eq. 2.5 for D in the region of 10^{-8} to 10^{-7} cm^2/sec and t in the region of 10^3 to 20×10^3 sec, while by plotting eq. 2.5 for \bar{C}_{cr}/C_o in the region of 1 to 2 and for D in the region of 10^{-8} to 10^{-6} , yields figure 2-4. By plotting eq. 2.6 for $\frac{\Delta t \times D}{\pi a^2}$ in the region of 0 to 1 and $\Delta \frac{C_{cr}}{C_o}$ in the region of 0 to 2 yields figure 2-5. The graphs 2-2, 2-3 show the critical time for a crack to propagate for $a = 0.085$ cm, if \bar{C}_{cr}/C_o and D are known. The curve that corresponds to the \bar{C}_{cr}/C_o can be obtained by interpolation from the already marked curves. Figure 2-4 is similar to figures 2-2 and 2-3 in a sense that it is drawn for $a = 0.085$ and knowing critical time and diffusion coefficient the ratio \bar{C}_{cr}/C_o can be found. Figure 2-5 shows how the variation of $\Delta \frac{C_{cr}}{C_o}$ affects the variation of the critical time with known \bar{C}_{cr}/C_o , a and D.

According to Matsuda *et, al* [8, p. 230], the critical hydrogen concentration for weld metal of HY-130 weldments is something less than 0.5 ml/100g or 0.55 ppm [11, p. 171], for lower critical stress in the region of the yield point of the base metal. Also, Shackleton [41, p. 21] reports that the hydrogen content¹² that caused cracking in high strength steel weld metal with 70 – 90°C preheat, was in the range of 0.1 – 0.2 and 1.0 – 1.5 ml/100g, for filler metal electrodes having carbon equivalent to 0.78 and 0.70 respectively. From the above, a critical hydrogen concentration of 3 ppm can be assigned to high strength steel weld metal, accounting for any possible error.

¹²Hydrogen collected over alcohol i.e., not a very good measuring method.

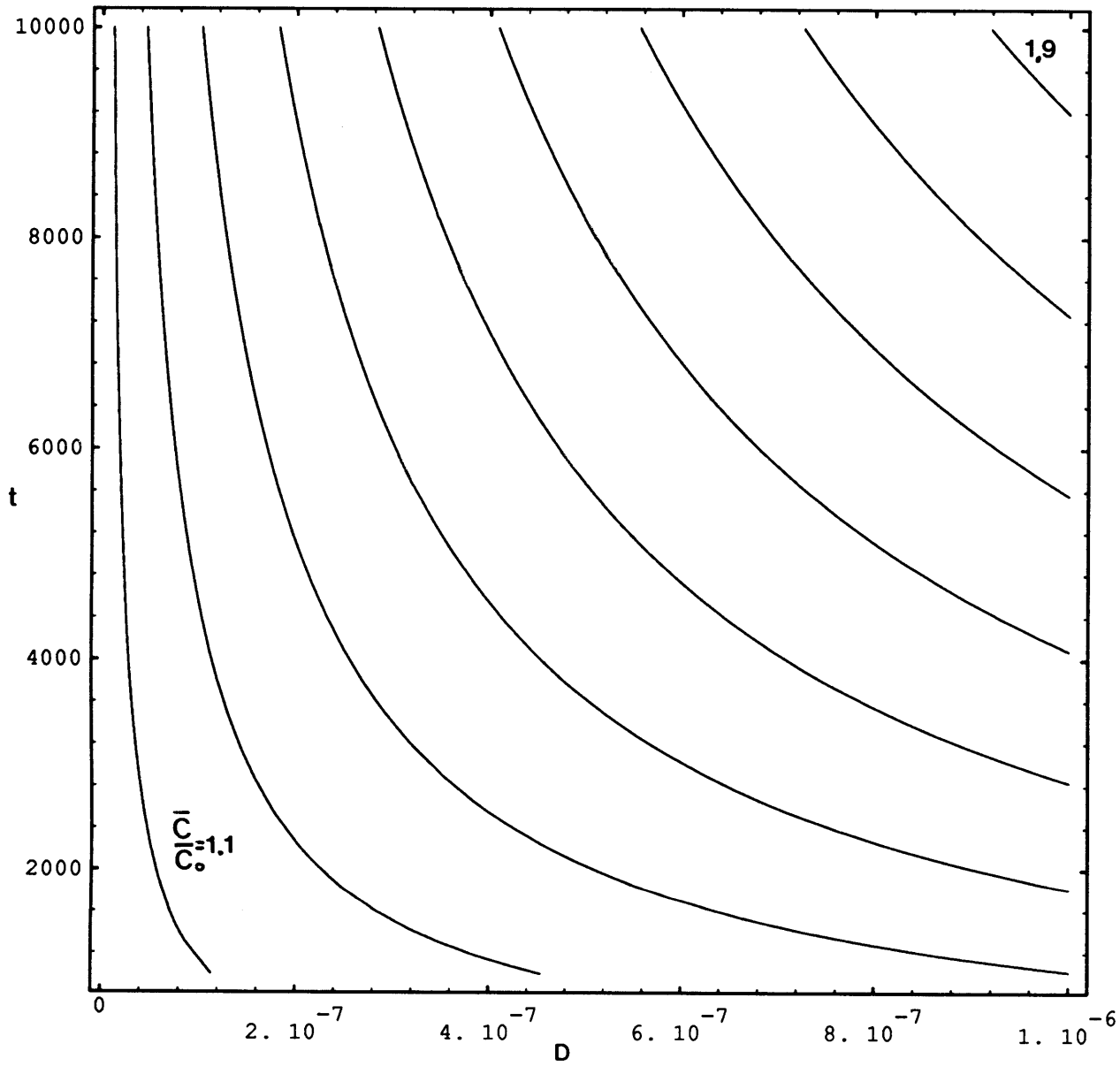


Figure 2-2: Variation of t vs D for Contours of C_{cr}/C_o from 1.1 to 1.9

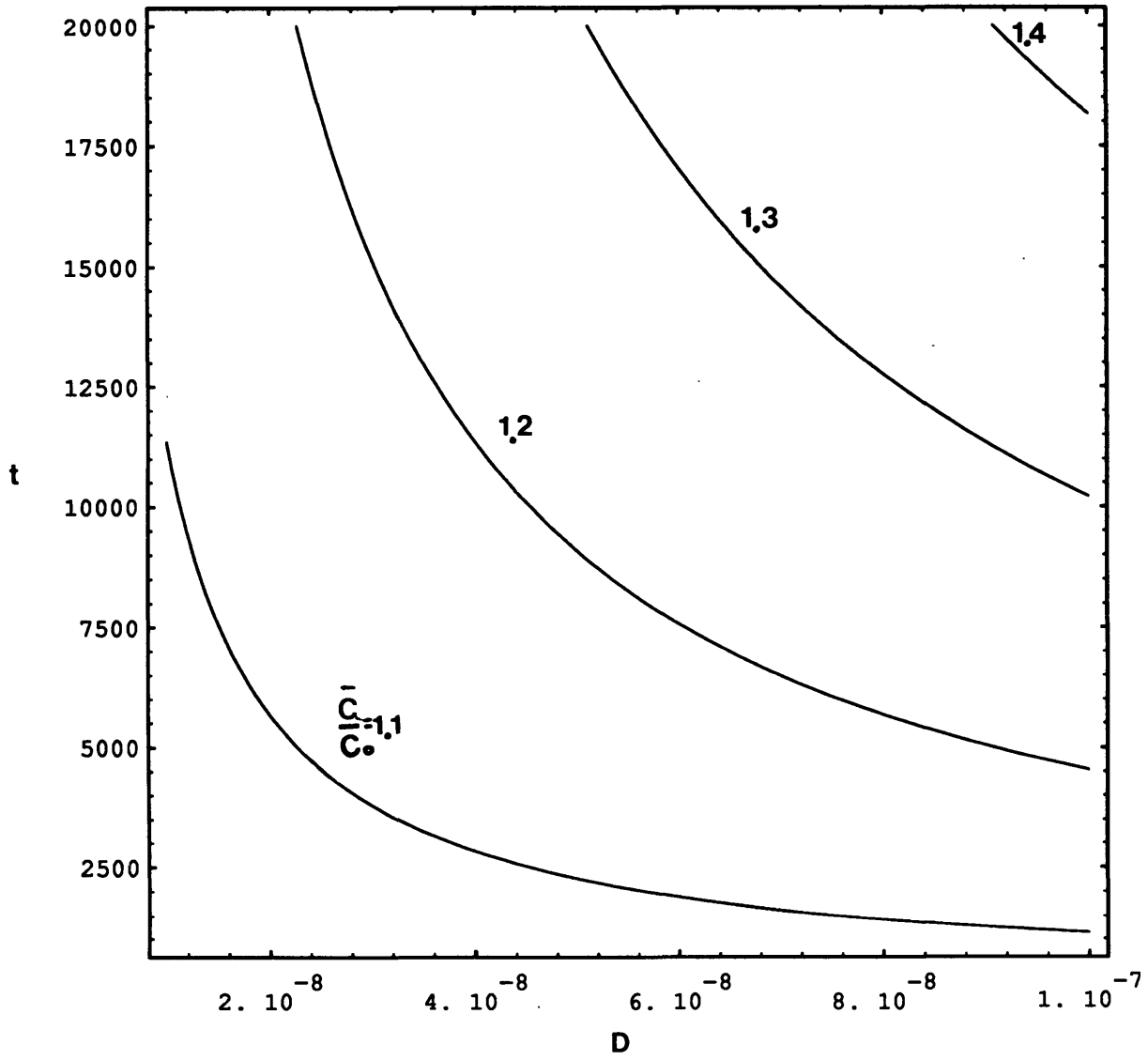


Figure 2-3: Variation of t vs D for Contours of \bar{C}_{cr}/C_o from 1.1 to 1.4

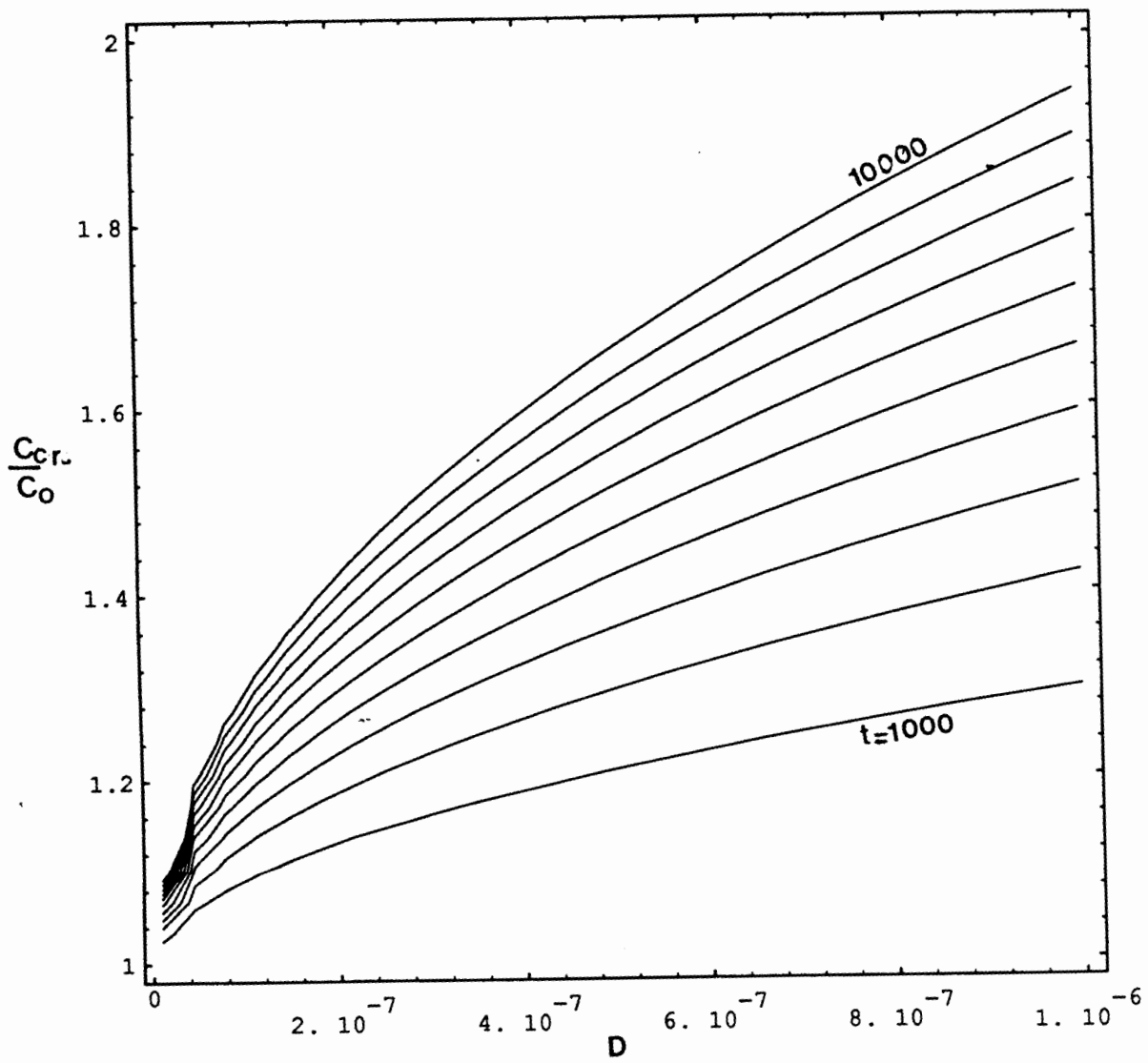


Figure 2-4: Variation of \bar{C}_{cr}/C_o vs D for Contours of t from 1000 to 10000

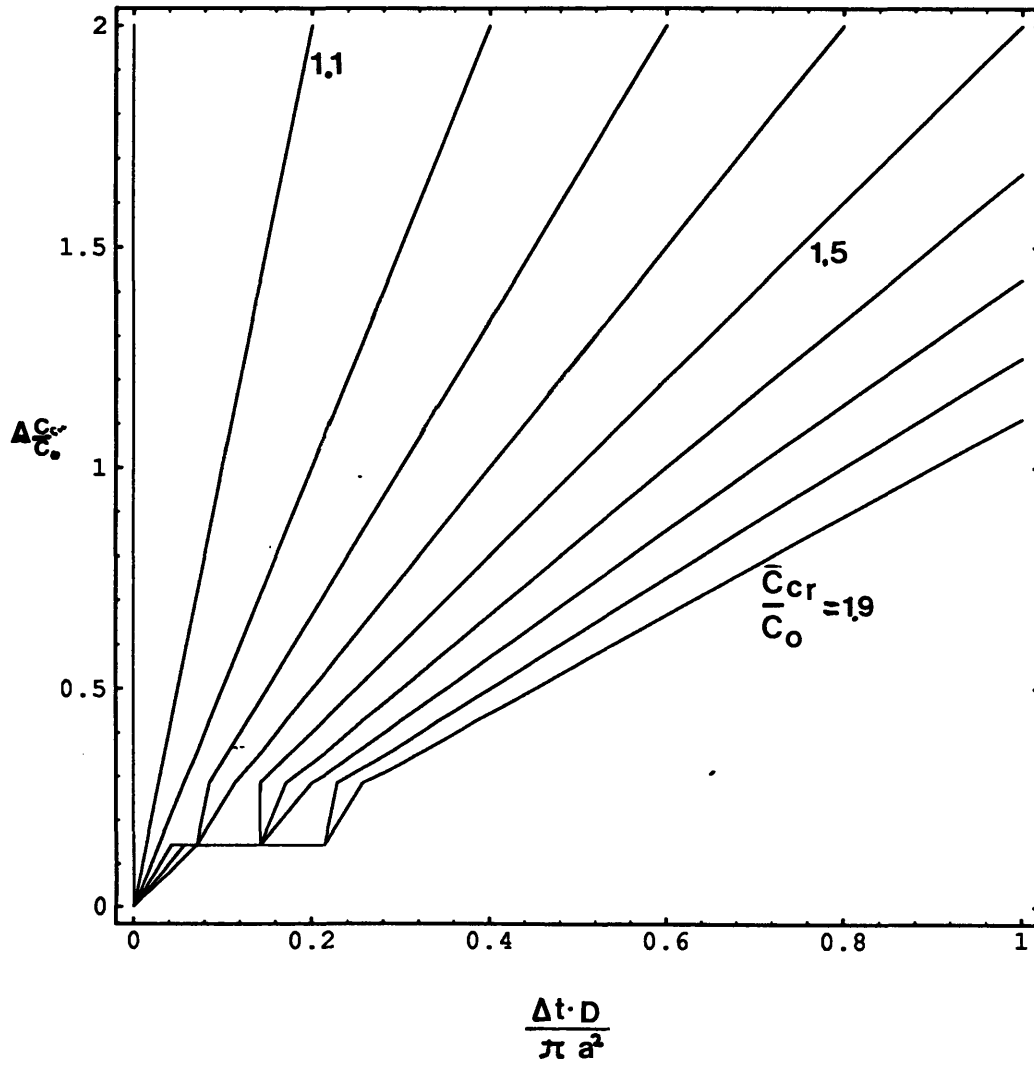


Figure 2-5: Effect of variation of $\Delta \frac{C_{cr}}{C_o}$ on time for Contours of $\frac{C_{cr}}{C_o}$ from 1.1 to 1.9

2.3 Discussion

Using the procedures described in section 2.2, I proceed to the following calculations making the additional assumptions:

- The hydrogen entering the weld metal¹³ is 2.5 ppm.
- The amount of hydrogen trapped by the inclusions is 1.6 ppm.

The amount of hydrogen-in grams-can be calculated from the equation:

$$M_H = C \times A \times k$$

where k is a constant, A is the area of the control space and C is the hydrogen concentration in ppm. The disk area is: $A_d = \pi \times r_p^2$. Following the above assumptions, the free hydrogen (not-trapped by inclusions) on the control space is:

$$m_f = (2.5 - 1.6) \times 1 \times k = 0.9 \times k \text{ grams}$$

The initial amount of the hydrogen on the disk-sink is

$$m_d = 2.5 \times A_d \times k$$

while the critical amount of hydrogen on the disk-sink is:

$$m_{dcr} = 3 \times A_d \times k$$

The amount of hydrogen that has to migrate to the disk is:

$$m_{td} = (3 - 2.5) \times A_d \times k = 0.5 \times A_d \times k$$

¹³The saturation value for hydrogen permeated in high strength steel specimen-according to Kim *et, al* [23]-is approximately 4 ppm, while due to the developed techniques regarding welding high strength steels [41, 5] and various factors-described in [11, p. 27], the entrance of hydrogen in the weld metal is limited. Therefore a value of 2.5 ppm seems quite reasonable.

The free hydrogen on the disk is:

$$m_{df} = m_f \times A_d = 0.9 \times A_d \times k$$

The amount of hydrogen just before the crack growth is:

$$m_{bcr} = m_{df} + m_{td} = 1.4 \times A_d \times k$$

Finally, the ratio $C_{cr}/C_o = m_{bcr}/m_{df} = 1.4/0.9 = 1.88$. Substituting this value of 1.88 in the equation 2.5, yields:

$$t_{cr} = \frac{2\pi}{D} \left(\frac{0.085}{2} (1.88 - 1) \right)^2 = \frac{8.789 \times 10^{-3}}{D}$$

Since D varies from 10^{-8} to 10^{-6} , the critical time is: 8.78×10^5 (244 hours) and 8.78×10^3 sec (2.48 hours) respectively. The effect of crack growth on the stress intensity factor is assumed to be negligible¹⁴ therefore, the plastic zone radius remains the same. From the observed crack length of one centimeter and the assumption that each single crack advance is $2 \times r_p$, for a 1 cm crack, it will take $\frac{1}{2 \times r_p} = \frac{1}{2 \times 0.085} = 5.9$ steps. Thus, the necessary amount of time will be

$$5.9 \times 8.78 \times 10^5 = 51.8 \times 10^5 \text{ sec (1439 hours)}$$

for $D = 10^{-8} \text{ cm}^2/\text{sec}$ and

$$5.9 \times 8.78 \times 10^3 = 51.8 \times 10^3 \text{ sec}$$

for $D = 10^{-6} \text{ cm}^2/\text{sec}$.

¹⁴On the one hand crack growth increases K-by increasing α but on the other hand it decreases K-by relaxing the residual stresses , based on the equation:

$$K = c\sigma\sqrt{\alpha}$$

where c is a constant, σ is the applied stress and α is the crack length.

Converting the above times to days yields 59.95 days and 0.5995 days (or 14.38 hours) respectively. In the case that no inclusions were in the weld metal then, the ratio $C_{cr}/C_o = m_{bcr}/m_{df}$ would be equal to $3/2.5=1.2$ and the respective (for the two limiting diffusion coefficients) times would become: $5.9 \times 4.5 \times 10^4 = 2.7 \times 10^5 \text{ sec}$ and $2.7 \times 10^3 \text{ sec}$ (or 3.1 days and 0.75 hour respectively).

Generalizing the above procedure for various values of \bar{C}_{cr}/C_o and D, the critical time for each step is shown in figures 2-2, 2-3, 2-4.

Let us suppose that after each time step, the uniform hydrogen concentration in the disk-sink changes. That can happen by variation of the rate that hydrogen migrates towards the new crack tip, due to stress relaxation-owing to crack opening, or due to dislocation sweeping [42]. This variation of the uniform concentration C_o , will cause a respective time variation as shown in figure 2-5. For example, if the initial $\frac{C_{cr}}{C_o} = 1.4$ and $\Delta \frac{C_{cr}}{C_o} = +0.4$ with $D = 4 \times 10^{-7} \text{ cm}^2/\text{sec}$ the time for the next crack growth step will increase by $\sim +11500 \text{ sec}$ (as can be found from figure 2-5).

Conclusion

In this study, neither the effect of many small cracks on the physical properties of the material [2] nor the binding energy of various types of traps [22]-affecting the solubility of hydrogen in iron, nor the effect of grain size on the critical stress needed for crack propagation-as shown in figure 22.24 in [38, p. 780], were included. Nevertheless, the hypothesis that the inclusions are responsible for the formation of a large population of small cracks is well supported by the fact that it will take too long for a crack to grow even to a length of approximately one centimeter in the presence of many trapping sites. Furthermore, hydrogen preferably moves towards closer crack nucleation sites causing the formation and limited growth of new cracks, instead of moving towards a specific crack tip. This phenomenon is attributed to the large variation of the diffusion coefficient at room temperature-as shown in figure 7 by Kiuchi *et, al* [22, p. 968] and figure 5.17 by Coe [5, p. 52]. It is also pointed out by Kiuchi *et, al* [22] that uncertainties and inconsistencies of experimental data for hydrogen solubility in BCC iron are due to:

- Non-Arrhenius behavior in the temperature dependence of the hydrogen solubility in bcc iron from what has been observed in a “perfect” bulk lattice
- Experimental uncertainties related to defects in specimen or experimental conditions
- Differences in metallographic structure and impurity levels

especially in low temperature regions. So a first step to predict a cracking resistant weldment, is by increasing the preheat temperature (i.e., the effect of preheat in

high strength steels weldments is more important than time, because of the higher effective activation energy). A more thorough study involving fracture mechanics and materials science theories could produce a model that predicts both qualitatively and quantitatively the factors that affect the hydrogen-induced crack initiation and propagation mechanisms. The value of such a model will be very much appreciated by the industry, since a large amount of money will be saved from the wastage of material and labor. Also, if unpredictability of the weld behavior is minimized it would contribute to lower the manufacturing costs.

Appendix A

Hydrogen Adsorption

A.1 One Hydrogen Atom per One Iron Atom

Assuming that one hydrogen atom sits on an iron atom and the latter is on the close packed plane (1 1 1). Referring to figure A-1, the number of atoms in the triangle is: $3 \times \frac{1}{6} + 1 = \frac{3}{2}$. The area of the triangle is: $A = \frac{1}{2}4\gamma\sqrt{16 \times \gamma^2 - 4 \times \gamma^2} = 4\sqrt{3} \times \gamma^2$. The number of atoms per unit area is: $\frac{3/2}{4\sqrt{3}\gamma^2} = \zeta$. The amount of hydrogen on each particle in grams per particle is:

$$\frac{\zeta \times A_i \times AW_H}{N_A}$$

where A_i is the area of the particle, N_A is the Avogadro's number and AW_H is the atomic weight of hydrogen. In the case of the iron lattice, with lattice parameter $\alpha = 2.86 \text{ \AA}$, it holds: $4\gamma = \sqrt{2}\alpha \implies \gamma = 1.011 \times 10^{-8} \text{ cm}$. The area of the triangle becomes $A = 7.0814 \times 10^{-16} \text{ cm}^2$. The number of atoms per unit area is: $\zeta = 2.12 \times 10^{15}$.

For $3.76 \times 10^{11} \frac{\text{particles}}{\text{cm}^3}$ and $A_i = 4.324 \times 10^{-9} \text{ cm}^2$, the amount of adsorbed hydrogen on the particles in a control volume of 1 cm^3 is:

$$M_H = \frac{2.12 \times 10^{15} \times 3.76 \times 10^{11} \times 4.324 \times 10^{-9}}{6.022 \times 10^{23}} = 5.72 \times 10^{-6} \text{ grams} \equiv 0.73 \text{ ppm}$$

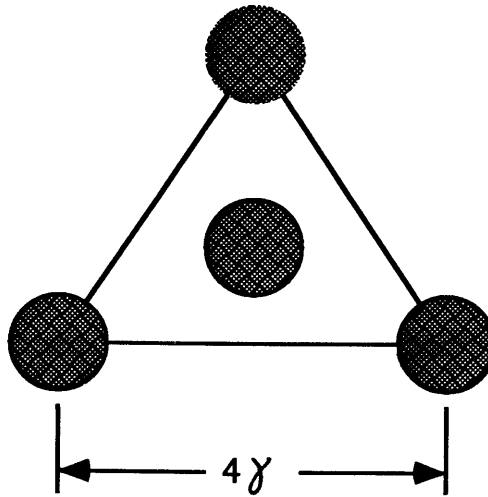


Figure A-1: The Closed Packed Plane of a BCC Lattice

A.2 Hydrogen Adsorption Using the Hydrogen Atomic Radius

The hydrogen atomic radius is: $r_H = 0.79 \text{ \AA}$. Each “sphere” of hydrogen covers $a_H = \pi \times r_H^2 = 1.96 \times 10^{-16} \text{ cm}^2$ of the area of the particle. Therefore, if the particle area is $A_p = 4.324 \times 10^{-9} \text{ cm}^2$, it can be covered by: $4.36 \times 10^{-9} / 1.96 \times 10^{-16} = 2.2 \times 10^7 \text{ atoms}$. The total amount of trapped hydrogen is:

$$\frac{3.76 \times 10^{11} \times 2.2 \times 10^7}{6.022 \times 10^{23}} = 1.37 \times 10^{-5} \text{ grams} \equiv 1.75 \text{ ppm}$$

Appendix B

Equations for Disk-Sink

Define as $\tau = \frac{\pi a^2}{2D}$.

- For $t < \tau$

Since $Q = \pi a^2 C_o (1 - \frac{2}{a} \sqrt{\frac{Dt}{2\pi}})$ is the amount of hydrogen that remains on the disk-source after time t , the amount of hydrogen that accumulates on the disk-sink after time t is: $Q = \pi a^2 C_o (1 + \frac{2}{a} \sqrt{\frac{Dt}{2\pi}})$. Dividing by πa^2 the equation becomes: $\bar{C} = C_o (1 + \frac{2}{a} \sqrt{\frac{Dt}{2\pi}})$. When I substitute $t = \tau$ in the above equation, it yields the maximum value for $\bar{C} = 2C_o$.

- For $t \gg \tau$

The equation for the amount of hydrogen that remains on the disk-source, is: $Q = \frac{\pi a^4 C_o}{4Dt}$. The amount of hydrogen that accumulates on the disk-sink is: $Q = \pi a^2 C_o + \pi a^2 C_o - \frac{\pi a^4 C_o}{4Dt} \implies Q = \pi a^2 C_o (2 - \frac{a^2}{4Dt}) \implies \bar{C} = C_o (2 - \frac{a^2}{4Dt})$. It can be seen that the above equation becomes maximum i.e., $\bar{C} = 2C_o$ only when the term $\frac{a^2}{4Dt} = 0$.

Appendix C

Inclusions

Liu *et, al* [29] reports data regarding volume fraction and population of fine particles having critical diameter-above which grain boundaries are not pinned by, for HSLA steels. Since no other data were available, I assumed that the critical diameter represents a sort of a mean diameter regarding the inclusions in the weld metal.

Referring to table 2.1 and taking the data from columns 3 and 4 (for diameter and density respectively), by using the equations:

$$N = \frac{\sum d_i n_i}{\sum d_i} = 3.76 \times 10^8 \text{ mm}$$

$$D = \frac{\sum d_i n_i}{\sum n_i} = 0.371 \text{ } \mu\text{m}$$

(where d_i and n_i are the respective diameters and densities for each particular case in table 2.1) the average density and diameter are obtained.

Appendix D

Initial Calculations

For the following calculations it is assumed:

1. The volume fraction of the inclusions 0.5%
2. The control volume is 1 *cm*
3. An average inclusion radius for higher strength steel $r_{hs} = 0.05 \mu m$
4. An average inclusion radius for lower strength steel $r_{ls} = 15 \mu m$

The population for the finer particles is: $n_{hs} = \frac{0.005}{\frac{4}{3} \times \pi \times r_{hs}^3} = 9.55 \times 10^{12}$, while the one for the inclusions in the lower strength steel is: $n_{ls} = \frac{0.005}{\frac{4}{3} \times \pi \times r_{ls}^3} = 3.54 \times 10^5$.

The available adsorbing surfaces are:

- $A_{hs} = n_{hs} \times 4 \times \pi r_{hs}^2 = 3000 \text{ cm}^2$
- $A_{ls} = n_{ls} \times 4 \times \pi r_{ls}^2 = 10 \text{ cm}^2$

for high and low strength steels respectively.

Using the equation developed in the section A.1 in appendix A,

$$M_{H_{hs}} = \frac{2.12 \times 10^{15} \times A_{hs}}{6.022 \times 10^{23}} = 1.02 \times 10^{-5} \text{ grams or } 1.3 \text{ ppm}$$

and

$$M_{H_{i_s}} = \frac{2.12 \times 10^{15} \times A_{hs}}{6.022 \times 10^{23}} = 3.52 \times 10^{-8} \text{ grams or } 0.005 \text{ ppm}$$

for high and low strength steels respectively.

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