The Relationship between Fugacity and Stress Intensity Factor for Corrosive Environment in Presence of Hydrogen Embrittlement

A. R. Shahani, E. Mahdavi, M. Amidpour

Abstract**—**Hydrogen diffusion is the main problem for corrosion fatigue in corrosive environment. In order to analyze the phenomenon, it is needed to understand their behaviors specially the hydrogen behavior during the diffusion. So, Hydrogen embrittlement and prediction its behavior as a main corrosive part of the fractions, needed to solve combinations of different equations mathematically. The main point to obtain the equation, having knowledge about the source of causing diffusion and running the atoms into materials, called driving force. This is produced by either gradient of electrical or chemical potential. In this work, we consider the gradient of chemical potential to obtain the property equation. In diffusion of atoms, some of them may be trapped but, it could be ignorable in some conditions. According to the phenomenon of hydrogen embrittlement, the thermodynamic and chemical properties of hydrogen are considered to justify and relate them to fracture mechanics. It is very important to get a stress intensity factor by using fugacity as a property of hydrogen or other gases. Although, the diffusive behavior and embrittlement event are common and the same for other gases but, for making it more clear, we describe it for hydrogen. This considering on the definite gas and describing it helps us to understand better the importance of this relation.

Keywords**--**Hydrogen embrittlement, Fracture mechanics, Thermodynamic, Stress intensity factor.

I. INTRODUCTION

HYDROGEN embrittlement and brittle fracture of materials that occurred by hydrogen diffusion are important phenomenon. The effects of hydrogen on various metals and use of metals that are well to tolerate them are discussed [1]. We should construct a physical model in order to solve diffusion equation to predict the treatment of crack growth. Crack growing and Stress corrosion cracking are caused by hydrogen emission around crack tip due to dissolve anodic reaction [2]. Major source of hydrogen is fossil-based hydrocarbons. Naturally, hydrogen molecular is gas, H2, is in the environment but, this is not able to diffuse in metals because, hydrogen in molecular form is too large to diffuse. Anodic reactions make diffusion possible. Whilst the reactions, hydrogen molecular (called dia-atomic) changed into small pieces (called mono-atomic). This kind of particles can penetrate in a surface and put themselves in lateral grain boundaries of materials. Line defects of hydrogen are produced in materials and accumulated strings of them along the defects. By pilling up them in materials its molecular is constructed again and causes to increase stress [1]. Mechanisms of diffusion are as follows [1]:

- ● Electro chemical evaluation
- ● Chemist option

Degradation of metal's the mechanical properties is the other effect of hydrogen while diffusing. It occurs in two ways, either hydrogen environment embrittlement (HEE) or internal hydrogen embrittlement (IHE) [3]. Jewett and Walter worked in the field. They tried to show differences between HEE and IHE under uniaxial tensile [3]. Moody and coworkers also investigated IHE and HEE of alloy 903 [3]. Takak u et al., Brinkman, Beston and Splichal et al. specified critical hydrogen concentrations for degradation of the mechanical properties both in the irradiated and unirradiated conditions [4]. Hybrid hydrogen storage vessel is new pressure hydrogen storage vessel has more advantages than traditional high pressure vessels and combined with different materials such as aluminum-carbon fiber reinforced plastic composition vessel and hydrogen storage alloy [5]. Hydrogen attack is occurred in two face, the first one is happened in ambient temperature as known "hydrogen embrittlement", another one is happened in high temperature known as "hydrogen attack". For prediction of mechanism around the crack tip it is necessary to solve a partial diffusion equation [2]. Diffusion occurs when there are gradient of concentration and stress as driving force. Corrosion fatigue and stress corrosion cracking are dominated by chemical anodic reaction, hydrogen embrittlement and dislocation mechanism and it is necessary to construct an exact physical law to definite hydrogen diffusion [6].

There are three basic models for modeling of hydrogen diffusion: Zapff-Tetelman model (hydrogen diffusion), Petch model (fracture energy), and Troiono model (introratomic band) [7]. A model can foresee the distribution of hydrogen atoms. Hydrogen assisted cracking depends on electrochemistry, stress, material composition and microstructure. In this model, gradient of reversible and irreversible trap sites are considered [8]. Another model defined the role of strain rate at a crack tip consisting a cylinder subjected to tension is parallel to cylinder axes [9]. In

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addition, researcher examined and analyze biaxial loading under the condition of small and long-scale yielding. This model analyzes the effect of biaxial loading on fracture toughness of pressure vessel [10]. Next model described the effect of hydrogen on stress intensity factor of steel that proposed by Liu in 1970 for elastic field on tip crack [11]. According to quell, the stress does not have any changes on diffusion coefficient but, it has effect on the solubility and chemical potential of two-component system. It is important to estimate the changes of chemical potential with stress to measure partial molar volume of hydrogen (PMV) at constant temperature. Li et al. have considered this problem as independent system between H and C without metal component [1]. In the following presented thermodynamic analysis of metal-hydrogen systems under the action of an external non-shear stress [1]. Beck et al. observed elastic stress does not alter the diffusivity of hydrogen in Irion and steel and effect of stress on solubility of hydrogen [10]. A model has been developed describing both the microscopic and macroscopic features of embrittlement due to dissolving or internal hydrogen [12]. Improvement of industry makes more familiar the man with using high strength steel and application of it [13]. One typical sample of application is pressure vessel.

One of the main concerning during an operation of pressure vessel (PV) is susceptibility of it to an embrittlement. For ensuring the required safety margin against a fracture, it should be tried with ASME Cod Section 3 and 4 [14]. Remaining of integrity of PV under severe operating conditions they should be designed with ASME Section 4 [15]. The material of PV containing of fluid is low-carbon steel and low alloy steel. These steels mainly contain Cr, MO or V as significant alloying element [16]. There are two important points to evaluate the condition of PV for operating. First is fracture toughness and second is the ratio of stress intensity factor to fracture toughness [17]. Hydrogen induced crack tip plastic deformation [18]. Hydrogen-assisted cracking (HAC), stress corrosion cracking (SSC) and applied stress all have profound effects on the details of embrittlement processes [18]. Hydrogen can facilitate the cracking of steels that occur in either of two ways, one is by a strain-controlled mechanism and the other one is by stress-controlled decohesion [19]. Stress corrosion cracking (SCC) and hydrogen embrittlement (HE) are related long-standing problems, commonly described under the name of environment-assisted cracking (EAC) [20]. Mastsumiya et al. have analyzed the hexagonal columnar dendrite model. In this work, the plate and columnar are considered [21].

II. HYDROGEN EMBRITTLEMENT

According to the ASME Materials Handbook lists five specific types of hydrogen damage to metals and alloys. These types are: 1) hydrogen embrittlement, 2) hydrogen-induced blistering, 3) cracking from precipitation of internal hydrogen, 4) hydrogen attacks, and 5) cracking from hydride formation.

Our aim is calculation of diffusion equation and fracture mechanics equation to guess the activity of hydrogen embrittlement in future. It is important for prevention of hydrogen embrittlement failure. We describe about the mechanism of diffusion. It is essential to know that for providing the conditions to make the material stronger and probably the best choice it for a special purpose and important for the failure analysis. While hydrogen diffusion occurring in dislocations because these have vacancies that hydrogen atom can enter them. Then at first, they must be trapped. Several types of sites were found to trap hydrogen such as grain boundaries, vacancies, voids, dislocations and so on. Trapping is divided into two types. Irreversible and reversible trapping are two kinds that depend on material properties the present of each one is changeable. The amount of Irreversible hydrogen can have effect on PMV because the definition of solubility done by that. Fig. 1 describes Hydrogen adsorption in metals exposed to a gaseous Hydrogen environment.

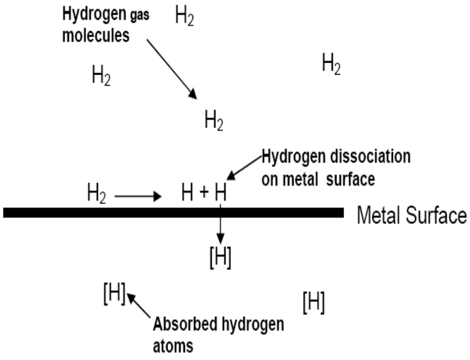

Fig. 1 Hydrogen adsorption in metals exposed to a gaseous Hydrogen environment

III. HYDROGEN ASSISTED CRACKING AND HYDROGEN FATIGUE

Hydrogen assisted cracking (HAC) phenomena is a process needs mechanical and chemical interactions at the same time. The characteristics of hydrogen assisted fracture are dependent on the metallurgical condition of the material, the hydrogen content and the exposure environment, temperature and loading conditions, including strain rate. According to studying and searching a lot in hydrogen damages and what the researchers told, a material either has contact with hydrogen or any other corrosion environment, phenomenon of electrical and chemical reactions of materials with its environment. Called corrosion, are unintended destructive. Hydrogen frequently leads to degrade material characteristics and diffuse through the grain-boundary and put itself into the lattice of materials. Simultaneously, diffusing of hydrogen and degradation of properties, crack stars growing until complete failure of whole material. Science of materials and profound mechanical studying of a microstructure in experimental method illustrate the procedure and mechanism of diffusion, degradation, and embrittlement and fracture to some extent but not completely.

Chemical reactions and embrittlement that follow with fatigue and fracture are the unavoidable and natural events definitely happened. Please, consider there is an environment consisting hydrogen as gaseous phase that has contact with metal surface. Therefore, hydrogen tries to diffuse it through whether splitting granular or grain-boundaries and failure it. Several kinds of failure (stress corrosion cracking, erosioncorrosion, corrosion fatigue, wear failure, liquid metal embrittlement, and hydrogen damage failure) can be attributed to corrosion.

While hydrogen contacts with surface of a metal, it needs energy to diffuse and cleavages of micro structure of metal. As mentioned, the molecule of hydrogen is big enough not to be able enter the metal and puts itself between the molecules and atoms of a metal. By chemical and electrical reactions and splitting molecule of hydrogen into two, atoms amount of energy released to help diffusing but it is not sufficient because another factor is temperature to support atoms to enter and cleavage boundaries. Depend on temperature there are two kinds of hydrogen embrittlement. The first is hydrogen attack and the second is hydrogen embrittlement. When damages of hydrogen happened at low temperature, this event called hydrogen embrittlement and if it has happened at high temperature called hydrogen attack. In this paper, the second one considered. After the atoms, diffused lines of defects are created and accumulate large amount of the atomies in these lines. By piling up them, molecules are constructed and stresses are produced. At the same time, properties of metal are such as ductility changed into brittle and this represents unstable crack growth and approaches the critical stress intensity to fracture the metal in the absence of hydrogen. As this event is happened at low temperature and due to fracture mechanics, fracture toughness is decrease and fast fracture is happened that it is very dangerous especially in industry.

Failure leads to kinds of damage. The most important reason of this phenomenon is crack growth. In Fracture mechanics, there are two various crack growing as follows:

- Fatigue crack growth
- Environmentally-assisted cracking

In this paper, we discuss fatigue crack growth and expand and illustrate the second one later. There is a very important issue for taking about is changing properties of especially metal. As said, when hydrogen molecular is diffusing, embrittlement is started. Experimental results and pervious searches show the plastic shape is not ignorable in spite of the fact that this region is smaller than elastic field.

Iv. Mathematical Equations

So, we need to see the treatment of a metal during time period of diffusion and guess what happens in future. Then it is essential to consider equation through that a designer can gain exactly the stress intensity factor as well as guess exactly when and where the metal damaged and failed. There are several parameters having a main role and have more effects on the event. So, three types of equations and solve them simultaneously to get one equation. They are should be seen in equations. In other words, the equations have to involve them definitely. On of these parameters is stress intensity factor. In this paper, we say there is an important relation between a fugacity and a stress intensity factor. According to the equations exist in this field of study, we try to obtain a new equation for solving the problem deals with the diffusion of hydrogen into surface of materials. This equation has several advantages. In this new work, you see the explicit relation that sufficient to have the fugacity of a gas such as hydrogen or combinations of several components of especial gases for replacing them into this equation and obtain the stress intensity factor. According to the work Larche and Cahn [22], they subtracted the value of stress times atoms' volume in the second side of the potential equation (4) to change it into the equal relation as it comes below. We do this work by subtracting the chemical coefficient instead of stress multiplies volume of atoms are diffused. Now, we prove that using gradient of chemical potential is the same as using gradient of electrical potential.

The mass flux of concentration is determined as follows:

$$J = -D\nabla C \tag{1}$$

Where, D is diffusion coefficient and C is concentration.

As we mentioned previously, the driving force to diffuse the gases into materials are caused by either the gradient of potential or the chemical's gradient of potential. In this paper, we try to consider it as a gradient of chemical potential. So, we have:

$$F = -\nabla\mu \tag{2}$$

where, μ is chemical potential.

According to definition mass flux and driving force, we can write:

$$J = CV = MFC = -(DC/KT)\nabla\mu \tag{3}$$

In this equation, M is mobility coefficient.

So, we said the flux only for gradient of concentration. On the other hand, the diffusion equation is:

$$\frac{\partial C}{\partial t} = -D\nabla J \tag{4}$$

Replacing equation (3) in (4), therefore:

$$\frac{\partial C}{\partial t} = D\nabla\left(\frac{C\nabla\mu}{KT}\right) \tag{5}$$

Also, Cahn and Larche's equation is as below:

$$\mu = \mu_0 + KT(\ln C + \ln\gamma) - \Omega\sigma \tag{6}$$

where, **Ω** is volume of atoms are diffused. So, by giving the gradient from (3), Eq. (7) is obtained:

$$\nabla\mu = -\Omega\nabla\sigma \tag{7}$$

Now, we replace Eq. (7) into Eq. (5) then, by giving gradient from this equation, we have:

$$\frac{\partial C}{\partial t} = D\nabla C - \frac{D\Omega}{KT}\nabla\cdot(\nabla\sigma\cdot C) \tag{8}$$

It is exactly the same as obtaining this equation by replacing electrical gradient as a driving force.

Also, thermodynamics proposes the below equation to show the relation between chemical potential and fugacity [23]. It says there is the following equation:

$$d\mu = RTd\ln f \tag{9}$$

The equation of $\frac{\hat{f}_i}{y_i}$ is substitute of fugacity f in Eq. (9). Therefore:

$$d\mu = RTd\ln\frac{\hat{f}_i}{y_i} \tag{10}$$

From both sides of the Eq. (10), we give integral between ideal and real gas conditions so, we have:

$$\mu = \mu_0 + RT\ln\left(\frac{f_i}{X_i} - \frac{\hat{f}_i}{X_i}\right) = \mu_0 + RT\ln\left(\frac{f_i}{\hat{f}_i}\right) \tag{11}$$

The Eq. (11) is correct only in absent stress reigns. When it used for presence of stress, it changed to unequal relation. So we add a value to the right side of this equation. As follows, we have:

$$\mu = \mu_0 + RT\ln\left(\frac{f_i}{\hat{f}_i}\right) + RT\ln\gamma \tag{12}$$

where:

f_i : The fugacity coefficient for i_{th} component in solution.

$\hat{f}_i$:The fugacity coefficient for i_{th} pure component in solution.

By putting equal (3) to (12) then:

$$RT\ln\left(\frac{f_i}{\hat{f}_i}\right) + RT\ln\gamma = KT(\ln C + \ln\gamma) - \ln(\Omega\sigma) \tag{13}$$

Replacing the concentration with pressure according to relation was said, obtained:

$$RT\ln\left(\frac{f_i}{\hat{f}_i}\right) + RT\ln\gamma = KT(\ln S\sqrt{P} + \ln\gamma) - \ln\Omega\sigma \tag{14}$$

The pressure has the following relation with stress intensity factor.

$$P = \frac{2K_I}{3\sqrt{\pi a}}(1+2\nu)\sigma \tag{15}$$

Replacing (15) in (13) instead of pressure then, obtained:

$$K_I = \left(\frac{\pi^{\frac{1}{4}}\gamma R\Omega(R-K)\sqrt{3}}{K^3TS\sqrt{2(1+2\nu)}}\right)^2 a^{\frac{1}{2}}\sigma\left(\frac{f_i}{\hat{f}_i}\right)^2 \tag{16}$$

For obtaining fugacity we can have wander Waal's equation. This equation is as follows [24]:

$$\ln\frac{f_i}{y_iP} = \ln\frac{\vartheta}{\vartheta - b} + \frac{b_i}{\vartheta - b} - \frac{2\sqrt{a_i}\sum y_i\sqrt{a_i}}{\vartheta RT} - \ln z \tag{17}$$

where:

ϑ : Molar volume.

a, b: Constants relating to component.

z: Compressibility coefficient.

y_i: Mol fraction of vapor.

By putting the Eq. (17) in (16) you can have stress intensity factor.

V. CONCLUSION

In this paper, a new equation that has an important role for diffusing phenomenon is obtained. Diffusion of the atoms into materials is done by driving force. We consider driving force is produced by chemical potential. According to the phenomenal of embrittlement of hydrogen, we consider the thermodynamic and chemical properties of hydrogen to justify and relate them to fracture mechanics. It is very important to get a stress intensity factor by using fugacity as a property of hydrogen or other gases. It is enough to have the g fugacity of a gas in infield pipeline. On the other hand, it is a new idea to see the problems of diffusion and has several advantages such as explicit relation between the fugacity of a gas or combinations of several components of especial gases and stress intensity factor. The main reason for noticing this phenomenon is having safety against the degradation, embrittlement and fast fracture. By getting stress intensity factor, you are able to obtain another factor such as critical life time, critical crack length and so on but not directly. Flexibility in this work is high because, you can see directly the properties of a gas have a contact to your materials for analyzing other factors.

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