Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 31
ISSUE 2
December
2008

The electric double layer in hydriding metals

K. Jamroziak [a,*], W. Jargulinski [b], J. Szelka [b]
[a] Combat Technology Department,
The General Tadeusz Kosciuszko Land Forces Military Academy, Wroclaw, Poland
[b] Department of Engineering,
The General Tadeusz Kosciuszko Land Forces Military Academy, Wroclaw, Poland
* Corresponding author: E-mail address: krzysztof.jamroziak@interia.pl

Received 23.09.2008; published in revised form 01.12.2008

Manufacturing and processing

ABSTRACT

Purpose: The effect of penetration hydrogen into fatigue load metals is widely investigated by many researchers. Hydrogen is the chemical element which plays negative role in fatigue durability of structures. It decides on fatigue brittle cracking. In the paper authors carry out an analysis of fatigue durability. Making use of naturally coming into existence the electric double layer phenomenon authors discussed the model of absorbing hydrogen into fatigue gap.
Design/methodology/approach: A proposed model of the mechanism of hydrogen absorption by metal was based on particle hydrogen and water vapor from the air.
Findings: It assumes that the EDL has crucial role in intercepting of polar dipole particles of hydrogen and water's vapor, especially in an already formed fatigue micro-gaps and gaps by effects of its electrostatic attraction force. The authors assume that the main source of hydrogen is water's vapor, and number of hydrogen dipoles is negligible.
Practical implications: The problems of metals' fragility/durability were also discussed in other papers in which author mainly tried to develop new methods of materials' production with the consideration of assumed fatigue durability.
Originality/value: Currently, in progress are works on proposing a model for hydrogen absorption by metal. Such approach to optimization in production and development of the new technologies is an essence of modern constructions that work in all variety of mechanical stress conditions.
Keywords: Environment and manufacturing innovations; Materials resistance; Hydriding metals

1. Introduction

One of the ways of increasing metals' durability is covering them with artificial plastic layers. The contemporary authors' works [1] [2] [3] [4] indicated existence of the electric double layer (EDL) at the metal-plastic contact. This layer, in its composition, mirrors principles of operation of the electrical condenser. The phenomenon of attraction of the opposite pole surface charges was used in problems of adhesion created at contact of metal with layer, with consideration of the EDL. Conducted experiments [5] [6] of the authors, were directed toward defining of hydrogen content in a dynamically stressed metals, and its effect on penetration mechanism with the assistance of EDL. This phenomenon was also researched by many scientists. Some of them in their research [7] [8] progressed to explain the mechanism of penetration of the gases (i.e. oxygen and hydrogen) into metals. It should be stressed that such influence on metal is negative. Especially hydrogen within metal is the reason of, so called hydrogen fragility. The problems of metals' fragility/durability were also discussed in papers [9] [10] [11] [12] [13] in which authors mainly tried to develop new

methods of materials' production with the consideration of assumed fatigue durability. Such approach to optimization in production and development of the new technologies is an essence of modern constructions that work in all variety of mechanical stress conditions.

2. The electrical double layer

At the contact of metal and a layer of artificial plastic exists naturally created EDL. The layer was experimentally defined in 1950s. It was found that in the layer, most often are created negative charges, and in a layer close to the surface of the metal – positive charges, or the other way around. In the vacuum, EDL concentrate itself in a cloud of electrons as a thin later over metal's surface creating negative charge. Moreover, in the structure metal-air we will also be dealing with EDL of the same configuration as in vacuum. To that conclusion lead fatigue researches [2] [5] in the electrostatic field for applied high voltages (over 5kV). To refer to the EDL metal-plastic matters in accordance with the publication [14] there are certain difficulties, that is, measures of EDL bear significant errors because of impossibility to complete removal of nitrogen layer that adhere metal's surface. Only indirect methods, in some ways, let accept thesis proving the existence of EDL at metal-air boundary. Upon own researches, there was found that air layerled to increase of fatigue durability, for both torsion and bending [15].

The applied electric field caused by high-voltage (2.0 kV) causes "pulling" the electrons from analyzed sample, which led to increase of EDL value in metal-air environment. It was noticed that polarization of EDL in the air is the same as in the vacuum, thus outside of metal is negative charge in shape of a cloud of electrons leaving metal. Therefore, at the metal-air boundary EDL reacts in a surrounding nearby electrical dipole-like elements, such as elements of water's vapor and hydrogen.

3. Hydrogen and metals' fatigue durability issues

The phenomenon of hydrogen penetration into a fatigue stressed metals is a subject of long-term researches of many scientists.

The Fatigue Life Forecasting of Modern Constructional Materials with the Use of Electric Double Layer [16], in which fatigue tests were conducted on samples of titanium alloy WT3-1, during which the samples were submitted to torsion and bending. Those researches were focused on defining of desorbed hydrogen volume on various planes, which results were shown on a graph (Fig. 1). On Figure 1,we can see that value Δp for surface layer (1) is much bigger than value Δp for not-loaded parts (3), in which the sample was mounted. The concentration of hydrogen in the zone (1) was estimated for 18 ppm. According to the authors [16], such large volume of hydrogen could come only from surrounding atmosphere.

However, another researcher [4] announced the values of concentrations of hydrogen and other substances in various parts of walls of a boiler apparatus. He noticed concentration of hydrogen in front of a top of a gap. The distribution of hydrogen around the gap is presented on Fig. 2.

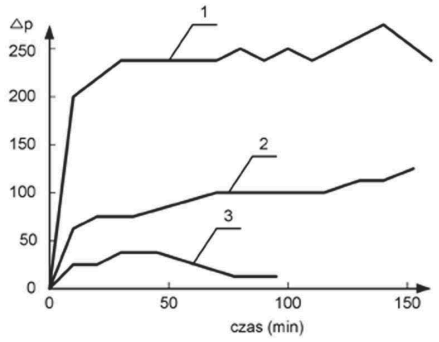

Fig. 1. Graphical presentation of the process of desorbed hydrogen volume change in function of the annealing time: 1–Surface layer, 2–middle layer, 3–holding parts of the samples [16]

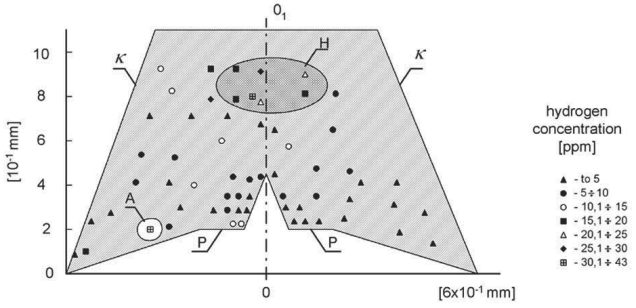

Fig. 2. The concentration of hydrogen distribution in the zone of gap in the inside of medium pressure turbine cylinder K-200-180 [4]

Based on a publication [17] mathematical relation of hydrogen penetration expressed in auxiliary form of the hydrogen concentration value is expressed as:

$$c_H = \frac{c_H^{(O)} \exp(-\gamma v_H \delta f / 4D)}{\sqrt{\Pi \delta V_H f / D} + 2\exp\left(-\gamma\left(2sD + V_H \delta f / 4D\right)\right)} \quad (1)$$

Where:
δ – Gap breadth,
$c_H^{(O)}$ – Hydrogen concentration for x=0,
γ – Experimental coefficient,
f – Cyclic load frequency,
V_H – Velocity of the gap widening,
D – Diffusion coefficient,
$s = V_H\left(\delta_m - \delta_o\right)/2R_oT$,
R_o – Gas constant,
δ_m, δ_o – Hydrostatic tension for x=m and x=0.

In sum, during the fatigue load of metals (work of construction loaded variably), hydrogen penetrates into metal from its surface, causing fragility phenomenon of this metal. Most of hydrogen concentrates before the top of the fatigue gap within plastic zone (max. approximately two times of the gap's breadth – Panasiuk's model). Together with the increase of the fatigue gap's length, the zone with absorbed hydrogen is moving in front of its top. The hydrogen fragility is a dangerous phenomenon for working construction.

3.1. Adsorption of hydrogen on metal

Gases such as hydrogen and water vapor set on metals causing adsorption. Depending on the kind of forces binding gas particle with metal, it is possible to distinguish physical and chemical adsorption. The physical adsorption binds with physical forces, mainly van der Waals forces and its duration is very short (approx. 10^{-8}s); whereas chemical adsorption is slower and uses chemical bonds, which base on the exchange of electrons at the boundary between metal and gas particles. Based on measurements (Fig. 3), Selwood found displacement of various gases' electrons on the nickel's surface. During adsorption of gas's particles on pure metal's surface, there is possible of occurrence of dissociation, that is, disintegration of the particle to atoms or simpler elements. According to Barrow, an H_2 particle when touches pure nickel's surface, it undergo dissociation to two atoms of hydrogen, taking two places on the nickel's surface, and creating, that way, bonds with metal's surface atoms. Such pure metal's surface is most often part of fatigue gap of extending cracking in the semi-cycle of stretching process, as well as a slide stripes, and dislocations exiting on the metal's surface. This type of surface is some kind of chemical catalyst.

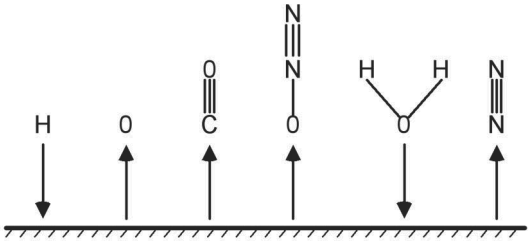

Fig. 3. Dislocation of various gases' electrons on pure nickel by Selwood

3.2. Mechanics of fatigue gap

During incubation period, as a result of cyclic load, are created dislocations, and they are shifted toward a surface, and they create slide's planes. When the concentration of dislocation reaches critical value [18] there occur sub-micro-cracks below the crack. During the phase of propagation, dominating micro-crack will change into macro-crack. In front of a top of the fatigue gap occurs plastic deformation [18], and each semi-cycle of stretching process is connected with increase of a fatigue gap length in top part, thus plastic zone moving further. In result, a new pure surface, that plays catalyst role, is created. The gap also pumps atmospheric gases. The time of opening of a gap is relatively long comparing the time of an adsorption. The volume of hydrogen H_2 in the air is slight. The main source of hydrogen is water vapor. It is strongly polar particle, positive charges of two hydrogen atoms and a negative charge of oxygen's. The negative charge of EDL on the metal's surface effects positive dipoles of hydrogen attracting them. On the bottom of the fatigue gap exists a congestion of EDL electron's cloud, the attracting force is strongest there. Such situation takes place during an opening of a fatigue gap. In this situation concurrently occur attracting effect of the EDL, a gap suction effect, and catalyst effect of newly created crack surface. The water's particles undergo disruption (dissociation), hydrogen undergo ionization (each is loosing an electron) and diffuse to metal, especially to favorable plastic zone. In a cycle of closing the fatigue gap, follows a mechanical disruption of other particles of water vapor. A probable mechanics of gap's operation is presented on Fig. 4.

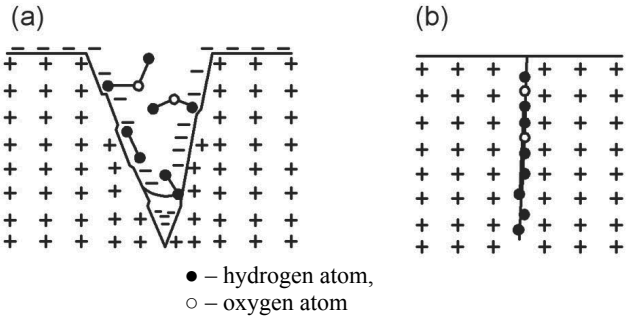

Fig. 4. The fatigue micro-gap: a – in a semi-cycle of stretching, b – in a semi-cycle of compression,

4. Proposed model concept

A proposed model of the mechanism of hydrogen absorption by metal was based on particle hydrogen and water vapor from the air. Schematically it is presented in Fig. 5.

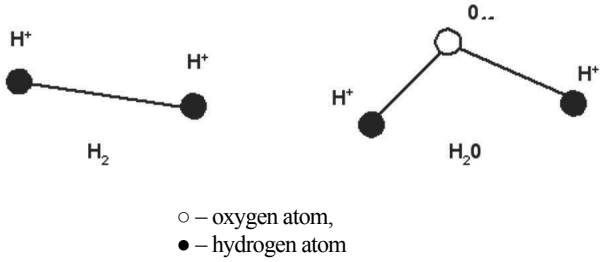

Fig. 5. Model of particle hydrogen H_2 and water vapor H_2O

On the surface of a model, a thin layer exists that consists of electrons of "electron gas," which are in constant motion. A magnified surface of metal in not flat, there is roughness that

resembles the Earth's hills and valleys, as well as faults and craters after travelling dislocations, which are created during metal load. Electrons of conductivity moving between ions network atoms and various interpolations. In case of meeting of imperfection in form of boundaries of seeds, gaps, empty spaces, electrons are going through them only if those objects are no bigger than eight parameters of a network. If on the metal's surface existing the fatigue micro-gap in shape of wedge, then electrons may partially fill the gap deforming in this spot electrons' cloud, and create concentration of electron's gas close to front of the gap. Such congestion of a negative charge within top of the gap attracts much stronger than another parts of a metal's surface, like positive charges i.e. hydrogen and water vapor. Two phases of absorption process were assumed:

- I – initial phase, similar to absorption process by Fujita [8],
- II– main phase, connected with absorption by micro-gaps and fatigue gaps.

It is assumed that both phases can occur concurrently, independently from each other in different parts on the surface of loaded metal. It should be mentioned that the best conditions presents freshly uncovered metallic surface. According to [8] absorption process was narrowed to oxygen absorption. In the concept of absorption model, was also assumed absorption of hydrogen, especially, because hydrogen ion is very small, thus can easier than oxygen drift between ions of metal that create lattice (Fig. 6).

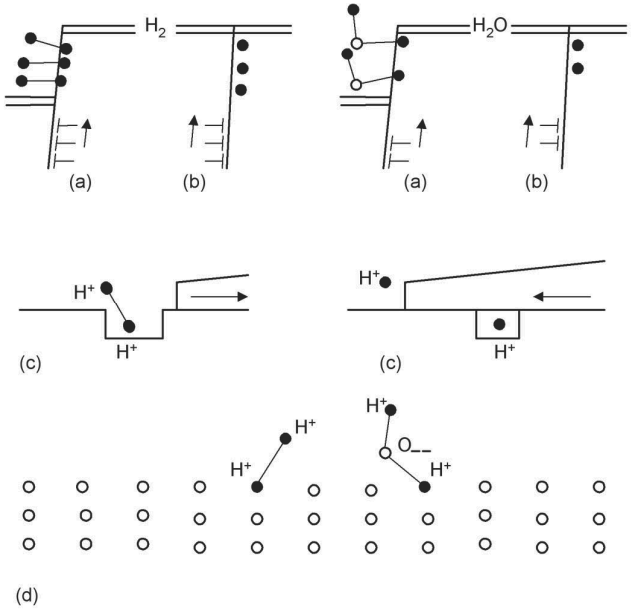

Fig. 6. Absorption of hydrogen (H_2 and H_2O) by Fujita's model [9] a – dislocation sliding movement, b – dislocation adversive movement, c – scheme of mechanical disruption of hydrogen particle, d – anchoring of hydrogen and water vapor in dislocation crater

From the analysis of the research on cyclic load of a sample (stretching – compressing of the close-to-surface layer of metal) is known that starts reciprocating motion of dislocation, and is created freshly uncovered metal's surface, on which negative charge of EDL, which electrostatic field attracts positive dipoles of H_2 and H_2O. According to the literature, water vapor and hydrogen give-away their electrons to metal, and can suffer dissociation. In the concept was assumed that hydrogen and water vapor are mechanically divided into a part that stays inside of metal, and a part that escapes into the air. From observation of absorption of hydrogen by fatigue gaps, it is noticed that absorption of hydrogen occurs in the form of particle hydrogen and as water vapor. A gap's work with a consideration of EDL (Fig.7) in a semi-cycle of stretching causes congestion of negative charges, and these charges' field attracts particles H_2 and H_2O, on freshly cracked gap's surface operates chemical catalyst, which leads to dissociation (disintegration) of particles. In a semi-cycle of compression, particles H_2 and H_2O are mechanically disrupted, and hydrogen and oxygen ions are drifting inside lattice of metal. Ionic oxygen may create thin layers of oxides on the inner surface of the gap; however, close to the top of a gap hydrogen operation prevails.

The most of hydrogen atoms in ionic form H^+(nucleus-proton) will be created in newly cracked zone of pure metal before the top of the fatigue gap, because appears:

- Hydrogen and water's vapor dissociation ,
- Mechanical damaging of hydrogen and water's vapor structure during closing of fatigue gap,
- Before the top of fatigue gap emerges highly deformed plastic zone that favors diffusion of a small ionic hydrogen H^+,
- Suction of opening gap and its diverging time in relation to the time of physical absorption.

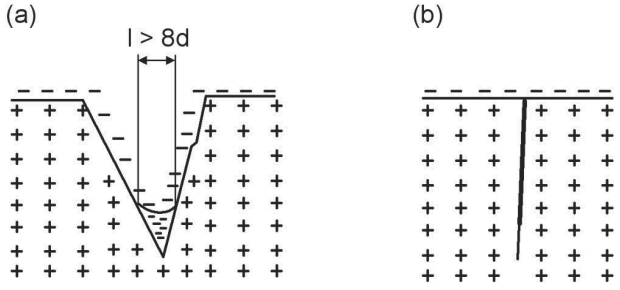

Fig. 7. A fatigue micro-gap: a – in a semi-cycle of stretching, b – in a semi-cycle of compression

5. Conclusions

Based on the publications of the matter and the results of own and other scientists' researches, were discussed main issues regarding metals' hydrogen brittle cracking, as well as effects of the EDL in hydrogenation of metals. After detailed analysis of the models of cracking in the fatigue gap concerning gases' penetration of metals, a new concept of different approach to such problems was proposed. It assumes that the EDL has crucial role in intercepting of polar dipole particles of hydrogen and water's vapor, especially in an already formed fatigue micro-gaps and gaps by effects of its electrostatic attraction force. The authors assume that the main source of hydrogen is water's vapor, and number of hydrogen dipoles is negligible. The tests results bring the following conclusions:

1. Together with broadening of the fatigue gap, the zone with absorbed hydrogen moving before its top. The hydrogen brittle cracking poses significant danger for loaded construction.
2. The faults and craters of dislocation appearing on newly uncovered sliding stripes are the places where polar hydrogen and water's vapor particles adhere.
3. A clean (pure) and freshly uncovered metal's surface is a catalyst, and on its surface occurs adsorption and other catalytic reactions that lead to dissociation of water's vapor.
4. Newly created metallic surface before the top of fatigue gap, is a catalyst, with simultaneous suction of gases, in a semi-cycle of stretching.
5. The EDL electrostatically attracts positive particles of water's vapor and hydrogen, especially in proximity of the top of the gap.
6. In a semi-cycle of compression, occurs closing of the fatigue gap and mechanical dissociation of water's vapor to hydrogen oxygen ions.

Currently, in progress are works on proposing a model for hydrogen absorption by metal, and the results of these researches will be presented in future publications.

References

[1] W. Jargulinski, J. Szelka, Formation of a double electric layer on the metal-plastic boundary, Springer New York, Journal of Materials Sciennce 40/5 (2004) 702-705.

[2] W. Jargulinski, The Electrostatic Field and Metals Durability, Monograph, The General Tadeusz Kosciuszko Land Forces Military Academy, Wroclaw, 2006.

[3] D. Kocanda, Testing a Short Fatigue Cracks, Monograph, University of Technology, Bydgoszcz, 2000.

[4] Waynman, Moder state of the problem of hydrogen embrittlement of metal of TPP thermo-mechanical equipment of pre-and overcritical parameters, 3rd International Conference, Fracture mechanics of materials and structural integrity, Lviv, 2004.

[5] W. Jargulinski, et al., The Electric Field Influence On Metals' Fatigue Durability, Science Reports of The General Tadeusz Kosciuszko Land Forces Military Academy, Wroclaw, 2002.

[6] W. Jargulinski, J. Szelka, The Electric Double Layer And Metals' Fatigue Durability, 20th Mech. Symp. Fatigue and The Mechanics of Fracture, Bydgoszcz-Pieczyska, Specjal Journal (2004) 121-127.

[7] J. Szelka, et al., The dynamics of the Electric double layer in the field of stresses of metal collapsible constructions, Science Reports of The General Tadeusz Kosciuszko Land Forces Military Academy, Wroclaw, 2005.

[8] F.E. Fujita, Dislocation theory o the fatigue fracture of ductile metals, Science Reports of Research Institutes Tohoku University, 1954.

[9] H.R. Kemp, L.H. Keys, Characteristics of stress corrosion cracking in austenitics stainless steels, Metallurgia and metal forming 7 (1977) 259-300.

[10] Y.K. Prasad, P. Praveen, M. Lin, N. Jee Aik Design and development of computer aided knoeledge base system for non-symmetrical sheet metal forming process, Proceedings Global Congress on Manufacturing and Management, Santos, Brazil, (2006) 109-113

[11] P. Praveen, and Y.K. Prasad. A. Turong, Study of droplet behaviour in active control of metal transfer," In Brito, Caludio D. and Ciampi, Melany, Eds. Proceedings Global Congress on Manufacturing and Management, Santos, Brazil, (2006) 12-16.

[12] Buchacz, Sensitivity of Mechatronical Systems Represented by Polar Graphs and Structural Numbers as Models of Discrete Systems, Journal of Materials Processing Technology 175 (2006) 55-62.

[13] L.A. Dobrzański, R. Honysz, S.D. Fassois, On The Identification of Composite Beam Dynamics Based Upon Experimental Data, Journal of Achievements in Materials and Manufacturing Engineering 16 (2006) 114-123.

[14] S. Skiner, R. Savage, J. Rutzler, Eletrical phenomena in adhesion, Electron atmospheres in dieletrics, Journal of Appilied Physics 24/4 (1954) 438-450.

[15] K. Jamroziak, W. Jargulinski, Fatigue Life Forecasting of Modern Constructional Materials with The Use of Electric Double Layer, 9th International Conference, Computer Aided Engineering, Opencast Mining 4-5 (2008) 148-151.

[16] D. Kocanda, About a Possible Cause of Characteristic Development of Short Fatigue Cracks in Titanium Alloy WT3-1O, 9th Conference of The Mechanics of Fracture, Kielce, Specjal Journal (2003) 261-268.

[17] V. Panasiuk, et al., Influence of Hydrogen-Containing Environments on Fatigue Crack Extension Resistance of Metals, Wybrani Praci 1991-2001, Narodnaja Akademia Nauk Ukrainy, (2001) 258-296.

[18] M. Szata, Description of Development of Fatigue Cracking in Energetic Approach, Monograph, University of Technology, Wroclaw, 2002.