Diagram of plastic material transition into brittle state under hydrogen saturation

V I Mironov\textsuperscript{1,2}, I G Emel’yanov\textsuperscript{1,2} and O A Lukashuk\textsuperscript{*}

\textsuperscript{1}Ural Federal University, 19 Mira street, 620002, Ekaterinburg, Russia
\textsuperscript{2}Institute of Engineering Science, Ural Branch of the Russian Academy of Sciences, 34 Komsomolskaya street, 620049, Ekaterinburg, Russia

*E-mail: oldim96@mail.ru

Abstract. Major progress made in theoretically describing the behavior of a «hydrogen-metal» system still fails to unambiguously explain the phenomenon of hydrogen brittleness in metals. It follows that a phenomenological approach is appropriate to describe the transition of a plastic material into its brittle state with the growth of hydrogen concentration. A diagram for such a transition is plotted on the basis of known experimental data on how hydrogen affects mechanical properties of structural steels. It is intended for the purposes of predicting the behavior of fracture observed in elements of metal structures under peak overloads or normal operation.

1. Introduction

Hydrogen, as a rule, has a destructive effect on materials of metal structure elements, diminishing both their short-term and long-term mechanical characteristics. A phenomenon of hydrogen brittleness in steels is the most dangerous of them all, causing unpredictable damages to petrochemical equipment, railroad accidents or plane crashes [1-3]. And there is no agreement on what causes that brittleness. Several nonuniversal conjectures were given [4-6], which cannot predict the conditions under which the scenario of brittle failure is realized.

Therefore, it remains topical to determine the conditions for transition of an initially plastic material into the brittle state under hydrogen impact. Which is also true for a phenomenological approach based on tests run over specimens with different hydrogen concentration. A well-known diagram of A.F. Ioffe defines the conditions for transition of a material from its ductile state into a brittle one due to lowered temperature [7]. Below, the diagram of ductile-brittle transition with the rise of hydrogen concentration in a structural material is considered.

2. Diagram of ductile-brittle transition of 25HNMA steel under electrochemical hydrogen saturation

Tensile tests of hydrogen-saturated metal specimens show that when hydrogen concentration grows ultimate and yield strengths change ambiguously. Earlier papers concerning hydrogen impact on mechanical properties of structural steels and alloys note fall in ultimate strength and plasticity indicators, rise in yield strength, insignificant decrease in modulus of elasticity with the growth of hydrogen concentration in a metal. As an example, a monograph [8] could cited where data is given on how hydrogen concentration affects ultimate strength $\sigma_{\text{ult}}(c)$ and yield strength $\sigma_y(c)$ in steels of
grade 20 and chrome-nickel 25HNMA. The data helped to plot approximating curves for 25HNMA (Fig. 1) and find their intersection at $c_{br} = 12.5$ ppm. This point defines the concentration for ductile-brittle transition of 25HNMA steel under electrochemical hydrogen saturation. It is suggested to measure further fall in the strength on the relation $\sigma_y(c)$ since there is no physical preconditions for a strength rise:

\[
\sigma_{ul}(c) = 1042.7 - 0.666c - 1.383c^2, \\
\sigma_y(c) = 723.4 - 0.378c + 0.694c^2.
\]

![Figure 1. Diagram of ductile-brittle transition for 25HNMA steel.](image)

When specimens saturated with hydrogen up to $c_i$ concentration are stressed just one time, their fracture is preceded by significant plastic deformation, and at $c_s$ levels – fracture is brittle. Under prolonged testing at $\sigma_D = const$ stress levels, fracture of hydrogen-saturated specimens is also brittle if the condition of $\sigma_D \leq \sigma_{ul}(c_{br})$ is true.

Cited reasoning related to the behavior of fracturing and practical significance of the diagram in general are restrained due to conditions of running such an experiment. For example, there is no reason to believe that the value of $c_{br}$ obtained there is such a constant for the material which is independent of the hydrogen saturation method, temperature and form of a specimen, surface state and structure of the metal, and other factors determining the process of hydrogen diffusion. When the phenomenological approach is used, the conditions of an experiment are selected as much as possibly authentic to how and when a studied object is utilized. In that case, knowing $c_{br}$ concentration is useful for design purposes to prevent dangerous brittle fracture of a product.

Gaseous hydrogen and metals interact at higher temperatures and pressures in such devices which produce, transport or store the gas. In that case, data on how hydrogen affects material properties could be obtained by saturating specimens with hydrogen by means of the Sieverts' method.

In our tests on 09G2S steel, a specialized test bed was used [9]. Tubular specimens of 0.5 mm in wall width were tested in their initial state and after hydrogen saturation at pressures of 5 at and temperatures of 580°C and 900°C. Processing thin-walled specimens leads, in cross-sections, to uniform fields of mechanical stresses, temperatures and concentrations of hydrogen. Besides, a substantial part of a tested metal corresponds to a weakened surface layer actively affected by hydrogen.

Tensile tests on the steel in its original state and hydrogen-saturated specimens were run at room temperatures on a tensile-testing machine Instron 8801. Computerized diagram 1 in the coordinates of
force-lengthening in Fig. 2 was plotted for unsaturated specimens. Diagrams 2 and 3 were plotted for specimens which had been saturated beforehand at 580°C and 900°C temperatures, respectively. Duration of saturation (three hours) exceeds an estimated time for saturating a specimen with hydrogen found by solving a thermal-diffusion problem via the method proposed in [10].

According to the Sieverts’ law, rise in saturation temperature leads to increased ultimate concentration of hydrogen in a specimen. The obtained data indicates at a diagram of ductile-brittle transition for 09G2S steel different from the diagram in Fig. 1 by fall in both ultimate and yield strengths with increased hydrogen concentration. Thus, the method of saturation changes the diagram of ductile-brittle transition.

3. Using ductile-brittle transition diagram to calculate strength and service life of structural elements

Results of full-scale tests on many products of the engineering industry provide objective information on their strength and service life. But, due to high costs of such tests, the amount of data obtained is somewhat limited, and the results are not statistically reliable. Besides, instrument inspection of hydrogen concentration distribution within a structural element is virtually impossible. Therefore, to determine the concentration at a critical point of a stressed structural element, it is necessary to solve a related thermal-diffusion problem [10,11]. And to solve a mechanical problem which follows, computerized diagrams (similar those shown in Fig. 2) are rearranged within new coordinates.

Assume calculations gave, at a certain moment, hydrogen concentration at a critical point of a structure as $c_1 < c_{br}$. Then, according to the diagram, a single overload of the structure would lead to a local fracture after plastic deformation. A computerized diagram is converted on rules taken from the strength of materials to the coordinates of intensities for tangent stresses and tangent strains. A criterium of ductile fracture could be defined in terms of reaching such an intensity of tangent stresses at a certain point of a structure which would correspond to the maximum on the calculation diagram for a specific material. Fracture could have pores, intrusions, stratifications.

When $c_2 > c_{br}$, a diagram is plotted in the coordinates of intensities for normal stresses and strains. According to the diagram of ductile-brittle transition, a brittle fracture is predicted at a critical point of the structure when maximal stress intensity is reached on it. Fracture might be also in the form of a microcrack whose stability is determined by additional calculation from the theory of cracks.

In the case of constant operational load, a stationary state of hydrogen concentration at a critical point could be reached for $c_{st} < c_{br}$. Therefore, hydrogen brittleness would not threaten the structure. In the opposite case of $c_{st} > c_{xp}$, a local brittle fracture is possible. Catastrophic brittle fracture of the whole structural element is most highly probable when stresses and hydrogen concentrations are uniformly
distributed at a critical point. The condition of $c_{st} = c_{br}$ allows to estimate a safe service life of a structure if no hydrogen brittleness is evident. Naturally, all logical constructions stated above should be supported by a correct and experimentally checked solution of a diffusion problem on determining a field of hydrogen concentrations in a structural element. The main difficulty here lies in finding a diffusion coefficient, or rather its dependence on those many factors present [12,13].

Results of research published until recently on diffusion of hydrogen in iron and its alloys show that cited values of the diffusion coefficient for the same steel could differ vastly [13-15]. Temperature, gradient of stresses, material structure imperfection would make their own impact [15-17]. Improvement of calculation and experimental methods to find fields of hydrogen concentration in a solid should certainly lead to modification of the diagram for ductile-brittle transition under hydrogen saturation. It is possible that this diagram would be useful for analyzing factors which cause fracture of structures in contact with hydrogenous environment.

4. Conclusion
The diagram of transition into the brittle state for plastic structural materials under hydrogen saturation is considered in terms of a phenomenological approach. No physical mechanisms of the process are referred to, but they will be accounted for in further calculations for the concentration of hydrogen in structural elements and, therefore, in predicting the behavior of local fracture at a critical structural point of saturated materials. Since there is no strict theory of hydrogen brittleness of metals present, the diagram could be used to analyze cases of fracture in saturated structural elements under peak overloads or normal operation.

References
[1] Goltsov V A 1998 Materials science – significance and place in hydrogen economics Hydrogen Treatment of Materials: Proc. of Il Intl. conf. «VOM-98» pp 10-2
[2] Cracknell A 1976 The effect of hydrogen on steel J. Chem. Eng. (Gr. Brit.) 306 92–4
[3] Pavlovskiy B R, Gedike H, Kizinger R, and Holzakov N V 1992 Inspection of pipelines by intellectual shell-defectoscopes J. Labor Safety in Industry 3 15–8
[4] Orlov V A and Glikman LA 1965 Hydrogen impact on intercrystalline strength of steels J. Physical and Chemical Mechanics of Materials 3 299–305
[5] Poltavets P A and Treshchev 2006 On theory of plasticity for materials subject to hydrogen embrittlement J. News of Higher Education Universities. Construction 1(565) 18–23
[6] Morlett J G, Johnson H H and Troiano A R 1958 A new concept of hydrogen embrittlement in steel J. Journal of Iron and Steel Institute 189 37
[7] Ioffe A F 1974 Selected Works vol 1 (Leningrad: Nauka) p 326
[8] Galaktionova N A 1959 Hydrogen in Metals (Moscow: Metallurgizdat) p 255
[9] Mironov V I, Emel’yanov I G, Vichuzhanin D I, Zamaraev I M, Ogorelkov D A and Yakovlev V V 2020 J. Diagnostics, Resource and Mechanics of materials and structures 1 12-19
[10] Emel’yanov I G Mironov V I and Lukashuk O A 2019 Phenomenon of embrittlement in titanium shells from hydrogen exposure J. IOP Conf. Series: Materials Science and Engineering 537 022067
[11] Emel’yanov I G and Mironov V I 2018 Thermal diffusion problem of hydrogen saturation of a steel shell structure J. Vestnik PNIPU Mechanic 3 27–35
[12] Bekman I N 2016 Mathematics of Diffusion (Moscow: OntoPrint Publishing) p 400
[13] Karpov S A, Nikitin A V and Tolstolutskaja G D 2017 Degradation of iron and its alloys affected by hydrogenous plasma J. VANT 4(110) 3-16
[14] Baranov V P and Sergeev N N 2007 Kinetics of Fracture and Prediction of Service Life for Strained High-Strength Steels in Hydrogenous Environments (Tula: TGPU Publishing) p 210
[15] Rebiakov Y N, Cherniavskiy A O and Cherniavskiy O F. 2010 Deformation and failure of materials and structures under diffusion J. News of SUSU 10 4–16
[16] Yang F 2005 Interaction between diffusion and chemical stresses J. Materials Science and
Vlasov N M and Fedik I I 2006 Structural and impurity traps for hydrogen atoms *J. International Journal of Hydrogen Energy* **M31** 265-7