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Hydrogen Degradation of The Pressure Gas Tanks Materials After Long-Term Service

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Abstract. It is experimentally established that air-tested samples of degraded material showed tooth flow that disappears for tests in hydrogen. The main feature inherent in the studied materials are metastable and presence of more or less pronounced time- and temperature-dependent processes of structural relaxation, which reduces the total free energy of a thermodynamic system. The values of fracture toughness minimize the square deviation of experimentally obtained values drift from the theoretical curve corresponding to the exponential relaxation function.

Introduction

Traditional high pressure vessels for compressed hydrogen storage are made of low carbon steels. Their great popularity is connected with a sufficiently high mechanical strength during long term service in hydrogen. But after a certain time it is observed that hydrogen degradation occurs in materials and the safety of hydrogen storage decreases[1-9].

The goal of the present work is investigation of hydrogen degradation of materials of the pressure gas tanks after long-term use in view of their safety.

Experimental estimation of hydrogen degradation depending on the concentration of hydrogen in steel after its long use under permanent and repeatedly static loading has not been conducted so far. It should be noted that in modern power engineering there are devices that constantly work in gaseous hydrogen under high pressure and, after not more than 10 to 15 years of operation up to 30 percents of storage vessels of large capacity are withdrawn from the installations.

Materials and procedure

The object of investigation is low carbon steel (Table 1, 2). The Investigation of hydrogen degradation was made by the verification of mechanical properties after long term service in hydrogen. Specimens were taken from hydrogen 40-liter storage tank (length – 1340 mm, diameter – 219 mm, wall thickness - 10 mm , weight – 60…81 kg), which contained 6 m^3 of gas at a pressure of 150 atm and 160-liter storage tank ST 160-20 type (working pressure Pp =200 kgs/sm^2 (during service Pp =150 kgs/cm^2)) (length 1990 mm, diameter – 390 mm, wall thickness > 20 mm, weight – 1370…1410 kg). Therefore, there is a need for the evaluation of the capability of structural materials for pressure vessels to strore hydrogen. Such evaluation can be based on fracture mechanics. There is also need to formulate new requirements for documents that regulate the possible prolongation of pressure vessels use. These should take into account hydrogen embrittlement and resistance to subcritical crack propagation with the large margin of safety.

Table 1. Chemical composition of steels for hydrogen storage in the initial state

Steel	C	Si	Mn	Cr	Ni	S	P
45	0.42-0.45	0.17-0.37	0.5-0.8	0.25	-	-	-
30KhGSA	0.28-0.34	0.9-1.2	0.8-1.0	0.8-1.1	0.3	0.005	0.025

Table 2. Mechanical properties of steels for hydrogen storage in the initial state

Steel	Ultimate strength σ_b, *MPa*	Yeld strength, $\sigma_{0,2}$, *MPa*	Young Modulus, *E*, *MPa*	Elongation, δ, %	Reduction, ψ, %	Ipact toughness KCU, J/cm^2	Fracture toughness, K_{1c}, $MPa\sqrt{m}$	Brinell hardness HB
45	726	432	213	26	51	29.4 (+20^{0}C)	73.5	229
30 KhGSA	883	687	198	10	-	98. (+20^{0}C)	80.1	212

Results and discussion

Experimental test results concerning properties of materials (steel 45) for pressure vessels after long-term service in different environments have shown the deterioration of their main mechanical properties (Table 3).

Table 3. Experimental results of materials (steel 45) properties testing of pressure vessels after long service in different environments

N	Specimen diameter d_0, mm	Square F_0, mm^2	Length l_0, mm	Length l_1, mm	Length l_2, mm	Specimen diameter d_2, mm	δ, %	ψ, %	$\sigma_{0,2}$, MPa	σ_b, MPa	Fracture toughness, K_{1c}, $MPa\sqrt{m}$	Environment
1	5	19.625	33	59.1	65.4	4.1	19	33	451	726	61.8	20^0, 10 at.H_2
2	5	19.625	33	59.2	67.7	3.5	26	51	432	726	73.5	20^0, air
3	5	19.625	33	59.2	65	4.2	18	29	402	726	58.8	20^0, 13 at. H_2
4	4,9	18.85	33	59.1	66.3	3.3	22	55	412	745	77.2	20^0, air

Chemical composition and mechanical properties (Fig.1) of specimens made from the shell and bottom of pressure vessels of CR 6409010 type and hydrogen pipelines, made from low carbon were examined after long term service in hydrogen.

Random crystallographic orientation of grains and grain boundaries blocked action (especially wide angle) results in simultaneous plastic deformation in multiple systems sliding. Plastic deformation in such steels begins in grains oriented along the direction of applied tension, even before reaching the limit of macroscopic plasticity, before the grain boundaries following clusters of similar dislocations [5,8]. This leads, in turn, to the formation of stress feedback sign opposite to the applied force. As a result of the simultaneous start of plastic deformation in grains with different crystallographic orientation, the strain curve below the macroscopic elastic limit is parabolic.

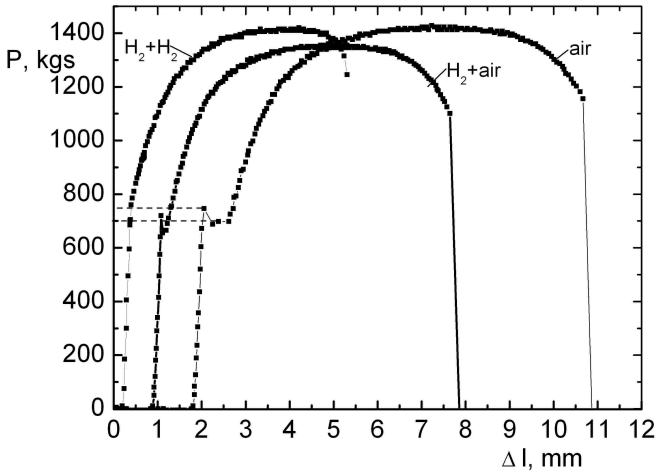

Fig.1. Loading - elongation curves of specimens made from steel 45 in the initial state in air (1), after long service (175,000 hours in hydrogen) in air (2) and after long term service (175000 hours in hydrogen) in high temperature hydrogen (3).

After reaching the macroscopic limit plasticity, plastic deformation is manifested in all grains. Plastic deformation is the result of uneven distribution of plastic waves, so-called Luders lines.
As a result of plastic deformation, accumulation of dislocations in some clusters activated the dislocation sources in neighboring grains, caused by the interaction of dislocations with stacking faults and dislocations in other slip systems. Impacts would be an increase of reinforcement. Increasing strain results in the saturation of grains with high density of dislocations and the formation of beans collar dislocation structure. Despite a long operation in the hydrogen atmosphere, on the curves obtained in air the upper and lower limit of plasticity are clearly separated. The limit of plasticity is tension necessary for macroscopic plastic deformation in the grains.
The upper limit of plasticity is associated with the separation of dislocations from the so-called Cotrell atmospheres, i.e. atmospheres of impurity atoms, such as C or N, which are located near the nucleus dislocation.
The lower limit of plasticity increases along with decreasing grain size according to the Hall-Patch equation

$$R_{ed} = \sigma_0 + k \cdot d^{-\frac{1}{2}}$$

where σ_0 – lattice friction stress, k – constant, d – diameter of the grain.
As a result of long term service, the residual volume of hydrogen absorbed by carbon steel from a finished cylinder was oscillating from 2.01 to 2.9 ppm (Figs.2 and 3).
The main feature inherent in the studied materials is the metastable state, which pronounced . the time and temperature dependent processes of structural relaxation. Such processes are usually referred to as degradation. In other words, degradation is a loss of material properties (monotonically increasing or flowing change in the controlled setting) as a result of a gradual and smooth transition to a thermodynamical equilibrium.
In terms of analytical description of the degradation transformations, the situation is further complicated by the studied materials often subject to external influence of temperature, hydrogen pressure and radiation fields, environment factors, mechanical stress, etc., which are not always conducive to an equilibrium.
In the aging process and the additional processing stage, achieve optimal properties..
That is why determining relevant physical laws and internal mechanisms of the degradation transformation is an important and urgent task.

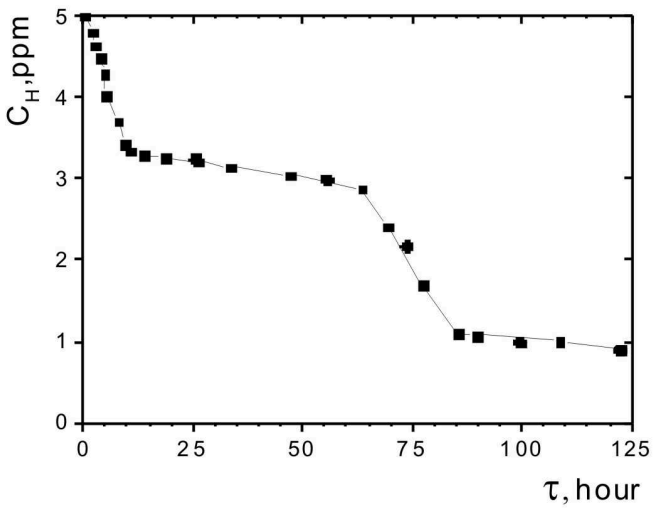

Fig.2. Modern methods of hydrogen concentration (C_H) in low carbon steel permits to establish influence of effective C_H (volume + surface + local) measured by extraction to glicerine, using LECO TCH 600 by means of infra red adsorption with specimen melting, as well as by discrete-point method using a laser mass-spectrometer "Eho-4M") permit to separate the next stage of hydrogen desorption: 1- from surface, 2- from defects, 3- from pores, 4 – from solid state.

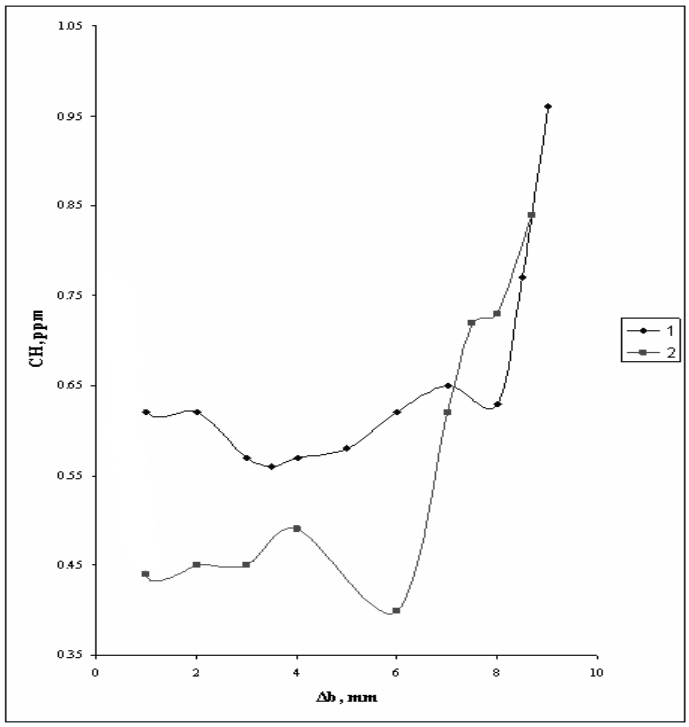

Fig.3. Distribution of local hydrogen concentration measured by a local mass spectrometer analysis using a laser probe after long term service (175000 hours) in room temperature hydrogen.

Typically, degradation drift of a controlled setting , ie the rate of change of this parameter in the degradation test is described by the equation:

$$\frac{d\eta}{dt} = -\lambda \eta^{\alpha} t^{\beta},$$

where α and β parameters define the type of relaxation function (RF) [6,7].

When α=1 and β=0, then kinetics of degradation is determined by the simple exponential function controlled by time parameter:

$$\eta(t) = ce^{-\frac{t}{\tau}}.$$

Experimentally observed kinetics of degradation (Fig.4, 5) is caused by the simultaneous contribution of several elementary degradation processes, each of which is exponential. In this case, the total degradation process is described by a linear combination of the individual processes.

If the rate of change of the controlled parameter in the process of degradation depends on time, i.e. parameter $\beta \neq 0$, then to describe its kinetics we can use the nonexponential function:

$$\eta(t) = c\exp\left[-\left(\frac{t}{\tau}\right)^{\kappa}\right].$$

This equation was first introduced more than 150 years ago (1847) by Kohlraush for the phenomenological description of the kinetics draining residual electric charge on a Leyden jar. [7]

Two groups of processes (were distinguished, mechanisms which correspond nonexponentially [7]. One group includes models that use the idea of dispersive transport, and the other - the model of hierarchically bounded dynamics that leads to the cross-correlation relaxation processes containing several consecutive stages.

For the purpose of adequate mathematical description of the kinetics, experimentally observed transformations were developed in a package of computer programs that allow the optimal RF (Figs.4, 5).

The parameters of the corresponding program picked up in a manner minimizing the mean square deviation (err), experimentally obtained values drift from the theoretical curve corresponding to monomolecular (exponential) or nonexponential RF.

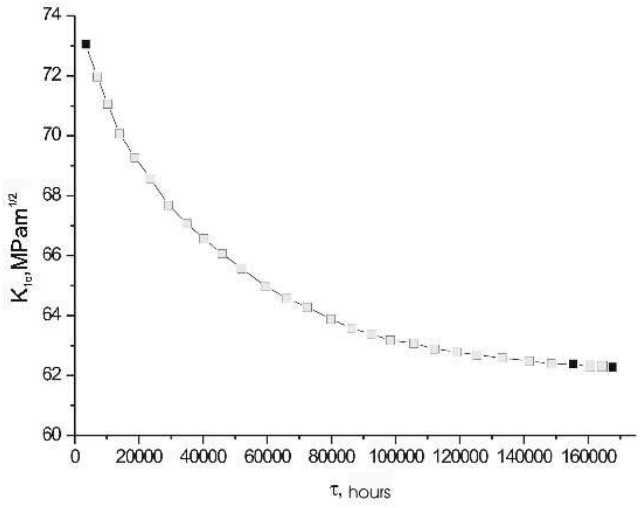

Fig. 4. Changing in time fracture toughness of specimens from long exploited (up to 175 thousand hours) walls of hydrogen cylinders, made of steel 45 (■–experimental, □–calculated data)

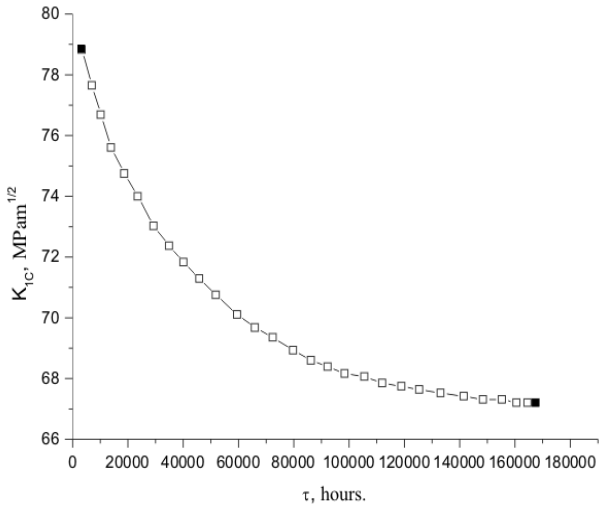

Fig.5. Changing in time fracture toughness of specimens made of long exploited (up to 175 thousand hours) walls of hydrogen gas holders, made of steel 30HhGSA (■–experimental, □–calculated data)

Conclusions

We improved the extraction method and determined the content of active hydrogen diffusion in samples of steel 45, which undergoes an intensive selection during the first 6 h. after saturation (maximum concentration is 2.8 ppm). The residual hydrogen content was determined by infrared desorption of fusion of the sample. Tested in air samples from a degraded material showed tooth flow, which disappears for tests in hydrogen.

The main feature inherent in the studied materials is metastable, i.e. the presence of more or less pronounced time- and temperature-dependent processes of structural relaxation, which reduces the total free energy of a thermodynamic system. They describe the loss of a particular material property (monotonically increasing or flowing change in the controlled setting) as a result of a gradual and smooth transition to a more thermodynamic equilibrium. The values of fracture toughness minimize the mean square deviation (err) from experimentally obtained values drift from the theoretical curve corresponding to the exponential relaxation function.

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