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HYDROGEN INDUCED INTERNAL CRACKING IN METALS CAUSED BY TRANSIENT THERMAL PROCESSES

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A quantitative model describing the behavior of cracks in metals filled with hydrogen gas is presented. Surplus filling of crack with hydrogen is caused by its diffusion flux due to transient thermal processes combined with internal heterogeneities in metals. The analysis of kinetics of hydrogen diffusion, precipitation into crack and its propagation is performed. The model may be employed to assessment of structural integrity under conditions of hydrogen destruction. An example of analysis of hydrogen induced delamination in weld-overlayed hydrotreating reactor pressure vessel is given.

1. Introduction

The effect of hydrogen on behavior of metallic materials has been well recognized as a significant source of risk of failure, especially in aerospace, power generating, and chemical industries. Till now numerous hydrogen-related degradation effects and modes of disintegration in materials and structures have been characterized and broad knowledge and experience have been achieved. Nevertheless, fractures of apparently unexpected types occasionally occur. Among them hydrogen induced damages in structures subjected to severe hydrogenation at high pressure – high temperature aggressive working environments may be noticed. In this respect it is especially worth to note hidden internal fracturing in structures protected from deleterious action of environment with coatings or overlays of more resistant materials. This kind of damage can destroy combustion chambers and other hot parts of hydrogen-fueled jet engines, hydrotreating reactor vessels, etc. It may seem surprising that flaws often arise there well after shutdown, i.e. when hydrogen environment was removed, structures were unloaded and cooled. This sort of hydrogen degradation according to the general engineering classification (cf Kharin and Fishgoit, 1993; Kronshtal and Kharin, 1992) is related to the class of phenomena of hydrogen destruction. It seems to be considerably less elaborated when compared with hydrogen embrittlement which has got an extensive treatment. The general rationale for this sort of hydrogen assisted fracture and its preconditions have been developed earlier (Kronshtal and Kharin, 1992). It was based on the analysis of creation of diffusion driving forces and hydrogen redistribution in metals caused by fast heterogeneous changes in its solubility. It was shown that just because of temperature variations in solids the zones of temporarily huge nonequilibrium hydrogen oversaturation can appear. Hydrogen concentration may exceed there its initial values to $5 \div 10$ and more times, and hydrogen activity – to several orders of magnitude. The amplitude of oversaturation depends on temperature variation rates, hydrogen absorption characteristics and sizes of mentioned solubility heterogeneities (Kronshtal and Kharin, 1992). Excessive hydrogenation of metal is the source of rising risk of hydrogen degradation.

It is naturally to expect that hydrogen can damage unloaded members due to its rising pressure in internal defects (pores and cracks) located in sites of oversaturation peaks. To evaluate such effects it is used to follow one of the two limit approaches. According to the first one (Goldshtein et al., 1985), filling of cracks with gas is estimated assuming that the defect is an unsaturable ("bottomless") sink of hydrogen. Thus, the conceivable amount of hydrogen in defect has no physical upper limit and, consequently, pressure increase is unlimited. The second one (cf Van Leeuwen, 1973) prescribes continuous maintaining of the equilibrium gas pressure in the crack corresponding to the concentration value calculated with no account for the effect of flaws in materials on diffusion. That is, the kinetics of mass exchange between the flaw and surroundings is ignored here. It is clear that both the ways lead to an overestimation of the pressure in cracks. Besides, they do not describe realistically the kinetics of crack pressure alteration which affects crack propagation and durability of a structure as a whole. The first approach is applicable only for short diffusion times whilst the second one is valid for infinitesimally small defects and slow transients. However, concerning the phenomenon of hydrogen destruction just the transient aspects of development of hydrogen supersaturations and concentration-pressure variations are of primary importance. Below the model of evaluation of coupled processes of hydrogen diffusion, crack filling with gas and crack growth is presented. It may be utilized as a part of realistic procedure of structural safety assessment and control. Example of numerical simulation related to disbonding cracking in weld-overlayed pressure vessel of hydrotreating reactor is described.

2. General model

In the previous paper (Kronshtal and Kharin, 1992) comprehensive analysis of the effect of transient temperatures and internal inhomogeneities in metals on hydrogen diffusion was presented. This was proved to be an important factor of raising risk of hydrogen destruction. It was shown that fast temperature variations can lead to a significant local increase of hydrogen concentration in the vicinity of steep gradients of hydrogen solubility in solids. However, Kronshtal and Kharin (1992) presented quantitative estimates which may serve only to detect potential structural integrity problems associated with danger of hydrogen destruction. They are not applicable to quantitative analysis of the fracture process governed by the hydrogen pressure within the crack. Therefore, progress in the modelling of hydrogen destruction needs additional quantitative relations that can match mutually interdependent simultaneous processes of diffusion, hydrogen precipitation into crack and crack growth.

Under conditions of heterogeneous hydrogen solubility the diffusion flux in metal is as follows (cf Kronshtal and Kharin, 1992)

$$\boldsymbol{J} = -DC\Big[\mathrm{grad}\Big(\ln\frac{C}{K_s}\Big) + \frac{Q}{RT}\mathrm{grad}T\Big] \tag{2.1}$$

where

$C = C(\boldsymbol{x},t)$ – volume concentration
$D = D(\boldsymbol{x},T)$ – diffusion coefficient
$K_s = K_s(\boldsymbol{x},T)$ – solubility factor
$Q = Q(\boldsymbol{x},T)$ – heat of transport for hydrogen in solid
$T = T(\boldsymbol{x},t)$ – absolute temperature,
R – is gas constant
$\boldsymbol{x}$ – vector of spatial coordinates
t – time.

The values of D, K_s and Q are material characteristics; they are supposed to be known as well as the temperature field in the solid. The factor K_s also enters the Sieverts' law, i.e. the equilibrium condition between hydrogen in gas phase under pressure P and dissolved in metal at concentration C

$$C = K_s\sqrt{P} \tag{2.2}$$

In the case of homogeneous material properties, when everywhere $K_s = K_s(t)$, Eq (2.1) may be reduced to the obvious Fick's diffusion law. Hydrogen solubility in metals depends on a number of factors. This may be described by the following expression

$$K_s = k_{s0}(\mathrm{Me}, \varepsilon_p) \exp\Big(-\frac{\Delta H(\mathrm{Me}, \varepsilon_p)}{RT}\Big) \exp\Big(\frac{V_H(\mathrm{Me})\sigma}{RT}\Big) \qquad (2.3)$$

where

k_{s0}	–	athermal part of the Sieverts' coefficient
Me	–	symbol representing chemical and phase composition of material
ε_p	–	value of plastic strain
ΔH	–	heat of solubility
V_H	–	partial molar volume of hydrogen in metal
σ	–	is hydrostatic stress.

Exponential character of K_s dependence on T suggests arising of great diffusion driving forces due to spatial and time alterations of the temperature field $T(x,t)$ itself and to heterogeneities of the values of $\Delta H(x)$ and $\sigma(x)$.

To complete the formulation of the diffusion problem the equation of mass balance must be used. It has the usual form

$$\frac{\partial C}{\partial t} = -\mathrm{div}\,\boldsymbol{J} \qquad (2.4)$$

To solve the problem of hydrogen diffusion, the material chracteristics, temperature field and usual initial and boundary conditions reflecting interaction of analysed solid with surroundings must be given. The role of cracks should be taken into account with the help of additional boundary conditions on their faces, to describe mass exchange between cracks and metal. At pressure values higher than about 0.1 MPa surface stages of hydrogen absorption by metals are quite rapid, i.e. they are not the rate limiting stages for mass exchange. This allows us to assume that during the whole process the equilibrium between hydrogen within a crack at pressure P and in the surface layer of metal along each of the opposite crack faces Σ_i $(i = 1,2)$ is maintained. This equilibrium is defined by the Sieverts' law (2.2). Therefore, on each crack face hydrogen concentration is $C_i = K_{si}\sqrt{P}$, where the pressure P is to be determined. It is related to the mass M of hydrogen in crack through the equation of state of a gas. In this paper we use the equation of state of an ideal gas $PV = (M/m)RT$, where V is crack volume, m is the molar mass of hydrogen. Volume V depends on geometrical parameters of a crack a_j $(j = 1,2,...)$ and on tractions causing crack opening. Here it is a crack pressure P (generalization for the case of other external loadings is obvious). Within linear elasticity crack volume is proportional to the pressure, i.e. $V = Pf_V(a_1, ...)$, where configuration function f_V presents crack volume at unit pressure. Using all above relations one can obtain the gas mass within the crack

$$M = \frac{m}{RT} f_V P^2 = \frac{m}{RT} f_V(a_j) \Big(\frac{C_i}{K_{si}}\Big)^1 \qquad i = 1 \text{ or } i = 2 \tag{2.5}$$

On the other hand, the change of the amount of hydrogen in the crack depends on hydrogen fluxes $\boldsymbol{J}_i$ on crack faces Σ_i $(i = 1, 2)$. As a result, the effect of gas filling the crack on diffusion will be reflected by the additional boundary condition on the crack surface $\Sigma = \Sigma_1 + \Sigma_2$

$$\frac{dM}{dt} = \int\limits_{\Sigma} (\boldsymbol{J}_1 \boldsymbol{n}_1 + \boldsymbol{J}_2 \boldsymbol{n}_2)\, d\Sigma \tag{2.6}$$

where $\boldsymbol{n}_i$ is a unit normal to Σ_i $(i = 1, 2)$ directed into the crack. Taking into account that hydrogen concentration on the crack faces is in equilibrium with gaseous hydrogen at the pressure P, Eqs (2.2), (2.5) and (2.6) give boundary conditions on the crack in the following explicit form

$$\begin{aligned} &\frac{C_1}{K_{s1}} = \frac{C_2}{K_{s2}} \\ &\frac{m}{R}\frac{d}{dt}\Big[\frac{f_V(a_j)}{T}\Big(\frac{C_i}{K_{si}}\Big)^4\Big] = \int\limits_{\Sigma} (\boldsymbol{J}_1 \boldsymbol{n}_1 + \boldsymbol{J}_2 \boldsymbol{n}_2)\, d\Sigma \qquad i = 1 \text{ or } i = 2 \end{aligned} \tag{2.7}$$

The last relations accomplish formulation of the model of hydrogen diffusion in solid accompanied by crack filling with gas. It is easy to see that the effect of cracks on diffusion will be greater when the value in left-hand part of the second of relations (2.7) becomes greater. In particular, this will occur with rising f_V, i.e. with larger cracks or their location nearer to the external surface of solid where their opening is less constrained.

In the form as described above, the model presents the closed set of equations of hydrogen diffusion in metal and its precipitation into cracks. It is applicable to evaluation of the gas pressure variations $P = P(t)$ in defects and to estimation of the conditions for their growth initiation with the use of conventional fracture mechanics techniques. It also allows us to estimate pressures $P(t)$ within propagating cracks as far as their geometry variations are given, i.e. functions $a_j = a_j(t)$ $(j = 1, 2, ...)$ are known. It is clear however, that this provides only partial solution to the problem of cracking because it can not predict the behavior of crack. To complete the formulation of the model of hydrogen destruction it is necessary to supplement equations of mass transfer with relations enabling one to determine crack dimensions a_j. This may be performed in two different ways depending on susceptibility of given materials at certain conditions (i.e. temperature and hydrogen pressure) to hydrogen embrittlement.

The first one is applicable when materials do not exhibit measurable subcritical crack growth because of hydrogen embrittlement (cf Pansyuk and Kharin 1990). In practice it may happen when either temperature is out of the range where this kind of hydrogen degradation is operative or materials of low susceptibility to hydrogen embrittlement are employed (e.g. low strength alloys). In this case the crack sizes are to be determined depending on pressure $P(t) = [C_i(t)/K_{si}(t)]^2$ ($i = 1$ or 2) from the obvious fracture mechanics equation

$$Pk_I(a_1, ...) = K_{Ic} \tag{2.8}$$

where

$k_I(a_j)$ – geometry dependent part of stress intensity factor K_I

K_{Ic} – crack growth resistance of material (fracture toughness).

Thus, in this case the model of hydrogen destruction consists of the initial-boundary value problem for differential equations of mass transfer (2.1), (2.4) and (2.7), supplemented with algebraic equation (2.8).

The second approach is appropriate when the effect of hydrogen on intrinsic metal resistance to the crack growth can not be neglected, i.e. when hydrogen embrittlement is significant. In this case the characteristic material curve which relates the crack growth rate ν to the stress intensity factor K_I and hydrogenation-environmental parameters, i.e. $\nu = \nu(K_I, P, C, T)$, must be employed. The latter should be determined either experimentally or using proper theoretical estimation (cf Pansyuk and Kharin 1990). Correspondingly, the model for evaluation of hydrogen destruction will be completed if the above mentioned system of diffusion-precipitation equations is supplemented with additional differential equations concerning crack geometry parameters

$$\frac{da_j}{dt} = \nu\Big[\Big(\frac{C_i}{K_{si}}\Big)^2 k_I(a_j), \Big(\frac{C_i}{K_{si}}\Big)^2, C, T\Big] \qquad \begin{matrix} j = 1, 2, ... \\ i = 1 \text{ or } i = 2 \end{matrix} \tag{2.9}$$

To prove the significant role of mass exchange between crack and surrounding metal on the driving force of hydrogen destruction cracking a numerical example associated with integrity assessment of hydrotreating reactor pressure vessel is presented below.

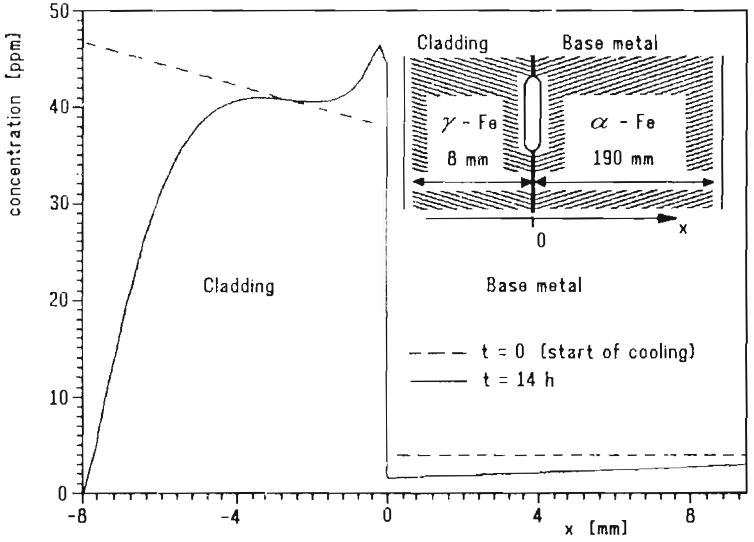

Fig. 1. Hydrogen concentration distributions through the thickness of hydrotreating reactor wall containing the crack of diameter $2a = 5$ mm at the clad/base interface

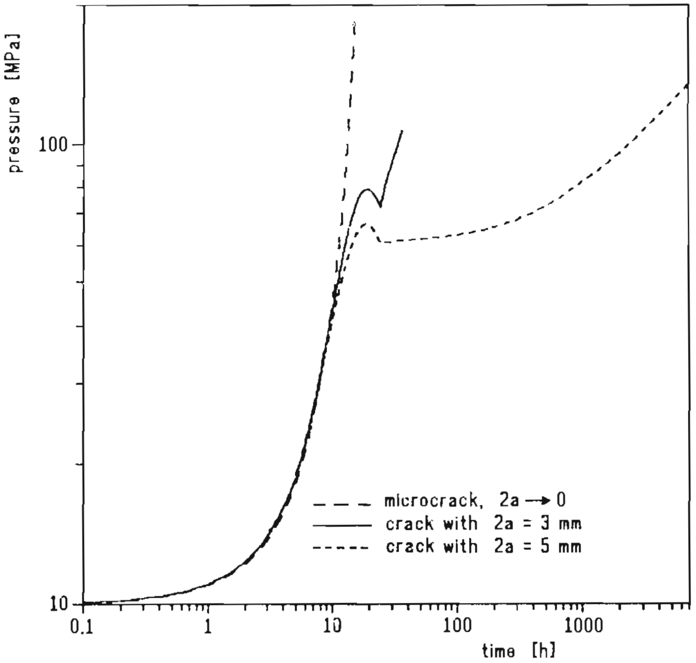

Fig. 2. Time variations of gas pressure within cracks of different sizes (the curve related to infinitesimally small crack presents the equilibrium pressure correspondent to the calculated concentration values in crack-free solid)

3. Numerical example

The problem under consideration is an estimation of a risk of hydrogen destruction in hydrotreating reactor manufactured of low-alloy ferritic steel 2.75Cr-Mo-V (α-Fe) of 190 mm thickness which is weld-overlayed with austenitic stainless steel 25Cr-13Ni ($\gamma - Fe$) clad of 8 mm thickness (Fig.1). After long-term service under conditions of high-temperature hydrogenation at internal reactor pressure $P_0 = 15$ MPa and temperature $T_0 = 723$ K the process is shutdown. The pressure is removed and reactor is cooled to an ambient temperature of $T_1 = 293$ K with the rate of $\dot{T} = 18$ K/h. It was proved by Kronshtal and Kharin (1992) that under this cooling regime temperature gradients through the wall thickness are negligible. Significant change in the ratio of hydrogen solubilities in α- and γ-iron K_{s1} and K_{s2} at cooling (to about 100 times) causes hydrogen redistribution fluxes in the reactor wall. Earlier (cf Kronshtal and Kharin, 1992) the analysis of hydrogen diffusion under these conditions has been performed basing on Eqs (2.1), (2.3) and (2.4), i.e. without taking into account the role of cracks. It was found that at the moment when the temperature T_1 was reached the concentration of hydrogen near clad/base interface achieved the value of $C^* = 180$ ppm. This corresponds to equilibrium hydrogen pressure of the magnitude of $P^* = [C^*/K_{s2}(T_1)]^2 = 11800$ MPa (it would be more precisely to say here about fugacity of non-ideal gas). It has already been mentioned above that this value may present only the upper limit for achievable pressures in cracks.

To estimate quantitatively the role of crack in the process described above the simulations were carried out with the use of the same initial and external-boundary conditions and material characteristics as in previous investigation (cf Kronshtal and Kharin, 1992). A penny-shaped crack of radius a was placed at the clad/base metals interface. From trivial solution for a crack in infinite solid (cf Parton and Morozov, 1978) the function $f_V = 16(1-\mu^2)a^3/(3E)$ was obtained. There Young modulus was taken to be $E = 200$ GPa and Poisson ratio $\mu = 0.3$ for both steels.

Non-linearity of equations of the proposed model prohibited the use of the earlier proved version (Kronshtal and Kharin, 1992) of realization of the finite element method. The finite differences technique turned out to be more convenient here. At each time step the nonlinear equation, being finite difference analog of relations (2.7), was numerically solved. To verify the algorithm of finite differences method the diffusion problem without a crack was first solved. The results were very close to that obtained with the finite element method (Kronshtal and Kharin, 1992). Further calculations were done accounting for the underclad crack at the interface (Fig.1).

As it follows from the obtained solutions (Fig.2) the developed generalized model predicts much less sensitivity of the reactor to hydrogen destruction in contrast to estimates of the commonly used concept of "equilibrium pressure" based on the solution to diffusion problem (2.1), (2.4) for crackless solid. Since in the performed simulations the effect of free surface of the solid on the crack opening (i.e. on the value of f_V) has not been taken into account, the results obtained may be considered to be a little bit overvalued. Nevertheless, they are much more realistic than estimates of the commonly used approaches. From the data presented in Fig.2 one may conclude that in this particular case the effect of gas pressure may be significant only at the stage of extension of a very small cracks. The role of pressure will diminish in course of their further enlargement for considered thermal scenario. It is worth to note, that this is not the general rule and the result depends strongly on material characteristics, mainly on hydrogen solubilities K_{s1} and K_{s2}, and on cooling rate $\dot{T}$.

4. Concluding remarks

The improved model for evaluation of hidden hydrogen destruction in nonhomogeneous structural members is presented. More realistic analysis of the joint effect of hydrogen diffusion in metal, crack filling with gas and crack growth leads to considerable quantitative differences when compared with known earlier simplified models.

In contrast to the obvious supposition, the severe working conditions at ultimate temperatures, pressures (loads) and aggressive environments may not be the most unfavorable for structural integrity. The performed investigation shows that analysis of structural safety requires to pay more attention to transient regimes which may cause the greatest risk of damaging. In addition to mechanical properties of materials usually employed for strength assessment, the characteristics of hydrogen solubility and diffusivity in metals and components play the decisive role in structural safety analysis. They are responsible for creation of stimuli to internal cracking.

The highest hydrogen pressures in cracks and its concentrations in the surrounding metal are reached well after cooling down of structural components to ambient temperatures. Thus, the severe hydrogen embrittlement should be expected despite the absence of preconditions for this kind of hydrogen degradation under working regimes. The structural integrity assessment procedure must include evaluation of susceptibility to hydrogen embrittlement.

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Wpływ wodoru na pękanie wewnętrzne w metalach, spowodowane przejściowymi procesami cieplnymi

Streszczenie

Prezentowany jest model rozwoju szczelin w metalach powodowany sprężonym wodorem. Wypelnienie szczelin wodorem następuje na wskutek obecności w metalu strumienii wodoru powstałych pod wplywem zmian temperatury oraz istnienia heterogeniczności wewnętrznej. Model może być przydatny do sprawdzenia bezpieczeństwa konstrukcji pracującej w warunkach spodziewanej destrukcji wodorowej. Podano przyklad zastosowania modelu do analizy rozwarstwienia płaszcza zbiornika z warstwami ochronnymi reaktora hydrokrakowania spowodowanego wodorem w ciągu schłodzenia go do temperatury otoczenia.

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