

# Two-continuum models of the dissolved hydrogen influence on strength of materials

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## Abstract

The main hydrogen influence mechanism in that case is diffusive redistribution of the hydrogen in tensile stresses zones (Gorsky's effect). The hydrogen material interaction increases the hydrogen bonding energy in those zones and decreases local mechanical properties of the material.

These effects can be described by a two-continuum model. The presentation is concerned with the model itself and its most important properties. The presence of the second continuum allows one to describe simultaneously the hydrogen embrittlement and superplastic transformations in the stress-strain diagram in the form of certain structural instability.

## 1 Introduction

The influence of small natural concentrations of hydrogen on material properties is very considerable. It becomes observable at the level of about a single atom per 50000 atoms of matrix of the matter.

On one hand, this influence of hydrogen can not be ignored since, in many cases, it is the only explanation of changes in material properties in time and under external loading. On the other hand, this influence is difficult to describe due to smallness of this factor and variety of consequences. For example, under change in the hydrogen concentrations by three-four times at the level of one atom per 10000 matrix atoms the mechanical properties of the material can change from brittleness to superplasticity.

An important role is played by the bonding energy of hydrogen in material. It is known that, inside the materials, hydrogen is found in traps with different bonding energies. In steels the total hydrogen content is 0.1-6 n.cm<sup>3</sup>/100g, while it is only hydrogen with a low binding energy that affects the strength, i.e. diffusively mobile hydrogen. In aluminum alloys the entire hydrogen diluted in the metal has a low binding energy - about 0.2-0.8 eV. The concentrations that are critical for the mechanical strength of weakly bound hydrogen in steels and aluminum alloys are similar - they are decimal ppm fractions. In aluminum alloys it includes the entire diluted hydrogen, while in steels it amounts to 5-10% of the total amount of diluted hydrogen.

Quite the contrary, the hydrogen with low bonding energy tends to zones of tensile stresses (Gorsky's effect [1]).

Accumulation of hydrogen in the destruction zone occurs both by the input from outside and by redistribution of natural hydrogen inside the material.

The well-known models of hydrogen influence for the materials properties are based on the experimental dependences [2]. These models describe only degradation of the material properties during hydrogen saturation.

There exists no approach which models the SMART-influence on properties of these structures. In contrast to the homogeneous materials, the nanocrystal materials in the presence of hydrogen demonstrate stabilization of their properties as hydrogen decreases the surface energy of crystals in material and prevent their increasing up to the micro size.

## 2 Two continuum model

The hydrogen with low bound energy is diffuse however its interaction with material is very weak. The high bound hydrogen interacts with material very intensively. This interaction is the main mechanism of the hydrogen stabilization and accumulation. The mechanical material properties degrade owing to this hard interaction.

This is the reason why suggested model must describe both the hydrogen diffusion and its interaction with material.

The mass equation for diffusely hydrogen inside the volume  $V$ :

$$m_H^- = \int_V \rho_H^- dV$$

Here  $m_H^-$  and  $\rho_H^-$  are mass and volume density of the diffuse hydrogen respectively. The differential form of this equation can be presented as follows

$$\frac{\partial \rho_H^-}{\partial t} + \nabla \cdot (\underline{v}_H^- \rho_H^-) = j_H^-$$

Here  $j_H^-$  denotes the mass flux density and  $\underline{v}_H^-$  is the velocity of hydrogen particles. In terms of the concentration  $N_H^- = \rho_H^-/m_H$  this mass balance equation has the form

$$\frac{\partial N_H^-}{\partial t} + \nabla \cdot (\underline{v}_H^- N_H^-) = \frac{j_H^-}{m_H}$$

The bound hydrogen obeys the same equation of the mass balance:

$$\frac{\partial N_H^+}{\partial t} + \nabla \cdot (\underline{v}_H^+ N_H^+) = \frac{j_H^+}{m_H}$$

Here  $N_H^+$ ,  $\underline{v}_H^+$  are the concentration and particle velocity for bound hydrogen (and bounded with them material particles).  $-j_H^- = j_H^+ = j$  is the redistribution flux inside the material. Since the concentrations are low we can assume a linear dependence for this flux.

$$j = \alpha N_H^- - \beta N_H^+$$

This equation describes the hydrogen redistribution over the different bound energy levels. The equation of dynamics for the material (first continuum) is

$$\nabla \cdot \underline{\underline{\tau}} = (\rho_0 + \rho_H^+) \dot{\underline{v}}_H^+ + j \underline{v}_H^+ + \underline{R}$$

Here  $\underline{\underline{\tau}}$  the strain tensor and  $\underline{R}$  is the force of interaction between the continua.

Only the spherical part of strain tensor is important for the second continuum (the diffuse hydrogen). This spherical part is characterised by pressure  $p$ . Then we can set the dynamic equation as

$$-\nabla p = \rho_H^- \dot{\underline{v}}_H^- - j \underline{v}_H^- - \underline{R}$$

The hydrogen particles velocities are very low because the hydrogen diffusion has time constant of the order from few hour to years. Hence we can put the dynamic equation in the form

$$\nabla \cdot \underline{\underline{\tau}} = (\rho_0 + \rho_H^+) \frac{\partial \underline{v}_H^+}{\partial t} + j \underline{v}_H^+ + \underline{R}$$

$$-\nabla p = \rho_H^- \frac{\partial \underline{v}_H^-}{\partial t} - j \underline{v}_H^- - \underline{R}$$

The interaction force is proportional to the difference in the continuum particles velocities

$$\underline{R} = \underline{A} \cdot (\underline{v}_H^+ - \underline{v}_H^-)$$

The tensor  $\underline{A}$  is determined in terms of such material properties as crystal grain surface area and crystal boundary volume.

The strain energy is known to have two parts, namely those of the volumetric deformation and shear energy. The Gorsky effect means that the volume deformation energy determines the hydrogen diffusion and its interaction with material. So we can define the spherical part of the strain tensor  $\underline{\tau}$ .

$$\underline{\tau} = \sigma \underline{E} + \underline{S}$$

The dynamic equations have now the form:

$$\nabla \sigma = (\rho_0 + \rho_H^+) \frac{\partial v_H^+}{\partial t} + j v_H^+ + \underline{R} - \nabla \cdot \underline{S}$$

$$-\nabla p = \rho_H^- \frac{\partial v_H^-}{\partial t} - j v_H^- - \underline{R}$$

We can determine  $\underline{S}$  as linear elastic part of the strain tensor. The constitutive equation for spherical part should be

$$\sigma = E_\Sigma \varepsilon$$

$$E_\Sigma = \frac{E_H E_0}{n_0 E_H + n_H^+ E_0}$$

$$n_0 = \frac{N_0}{N_\Sigma}, \quad n_H^+ = \frac{N_H^+}{N_\Sigma}, \quad n_0 + n_H^+ = 1.$$

Here  $N_\Sigma$  is the full number of particles in elementary volume,  $N_0$  - the number of the particles connected by unspoiled bonds,  $N_H^+$  is the number of hydrogen particles attached to a lattice with the bonds by rigidity  $C_H$ . Further,  $n_0$ ,  $n_H^+$  are the concentrations of the above mentioned particles, respectively.

The equivalent elastic modulus for the lattice  $E_\Sigma$  can decrease essentially, since  $E_H \ll E_0$  ( $C_H \ll C_0$ ), and has a strong dependence on the concentration of the attached (bound hydrogen) particles  $n_H^+$ .

The number of the lattice settled hydrogen particles depends on the stress state of the lattice in every point and, generally, on time. The unknown functional dependence of  $E_\Sigma$  on  $n_H^+(\varepsilon, x, t)$  should be determined from model of the two-component continuum.

Substantiation of the theory of two-component continuum can be found in Ref. [3]; Here we present only the final results with some necessary explanations.

The state equation  $\sigma = \sigma(\varepsilon, n_H^+(\varepsilon, x, t))$ , can be presented in form

$$\sigma = E_0 \varepsilon \left[ 1 - \frac{n_H^+}{n_H^+ + n_0 E_H E_0} \right],$$

and the essential dependence of the stress state on concentration of the bonded hydrogen becomes evident.

The hydrogen concentration is described by equation for  $n_H^+$ .

$$\frac{\partial^2 n_H^+}{\partial t^2} + (\alpha + \beta) \frac{\partial n_H^+}{\partial t} + A \cdot D(\varepsilon_{st}) \left[ \beta \frac{\partial^2 n_H^+}{\partial x^2} + \frac{\partial^3 n_H^+}{\partial t \partial x^2} \right] = 0$$

Here  $A = C_H^2 k j$ ,  $\alpha$ ,  $\beta$  are constants and  $D(\varepsilon_{st})$  denotes the hydrogen diffusion constant.

This two equation are used for modeling the hydrogen influence on the  $\sigma(\varepsilon)$  dependence of the material.

The dependence (Fig.1) describes the material properties modification during the hydrogen redistribution within the material.

The part of the  $\sigma(\varepsilon)$  dependence with  $\frac{d\sigma}{d\varepsilon} < 0$  can not be realized. The growth of the  $\varepsilon > \varepsilon_{cr}$  causes to hydrogen embrittlement and destruction.

However the hydrogen saturation leads to decreasing of the breaking point  $\sigma_{cr}$ .

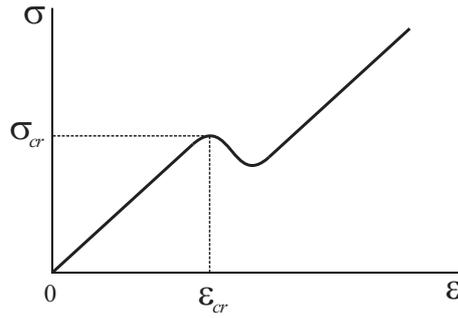


Figure 1:  $\sigma(\varepsilon)$  dependence of the material with hydrogen redistribution

The two continuum model describes the hydrogen redistribution in zones of tensile stresses. We can develop a finite element model for real structures if we take into account the outside hydrogen saturation.

The form of  $\sigma(\varepsilon)$  curve depend on  $\alpha - \beta$  ratio. For the case  $\alpha \ll \beta$  the form of  $\sigma(\varepsilon)$  is shown in Fig.2

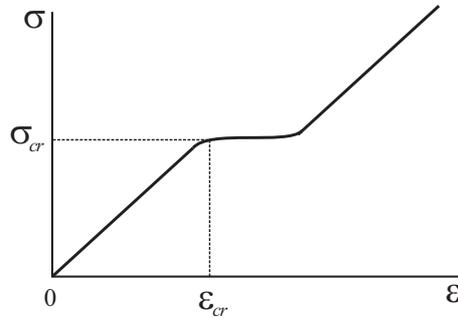


Figure 2:  $\sigma(\varepsilon)$  dependence of the material in case  $\alpha \ll \beta$

The plane of quasi plasticity changes the unstable part of the  $\sigma(\varepsilon)$  curve.

### 3 Discussion

Similar  $\sigma(\varepsilon)$  curves were observed in the experiments with titanium alloys with large hydrogen concentration. This effect was referred to as the superplasticity of the titanium alloys. The experimental  $\sigma(\varepsilon)$  curve for alloy VT20 is shown on the Fig.3.

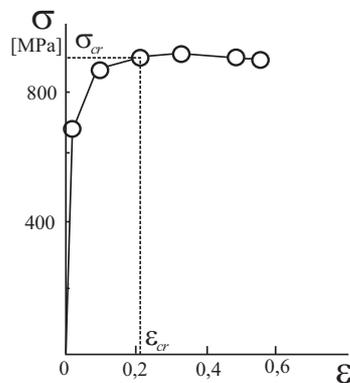


Figure 3:  $\sigma(\varepsilon)$  for VT 20 + 0.5% H<sub>2</sub> [4]

Our model describes only two hydrogen bound energy levels. In that case the loading process is reversible which is in contradiction with experimental data.

We can suppose that the hydrogen has three or more bound energy levels in the titanium alloys. The third energy level is the chemical bound (1.4 eV).

The experimental data confirms this hypothesis. The titanium alloys with hydrogen gives hydride nanoparticles under mechanical loading [5]. The average diameter of the hydrides is 50 nm.

## 4 Conclusions

A model is constructed which allows one to describe the kinetics of hydrogen in metals, and in particular to estimate the hydrogen transition from mobile into bonded state depending on the stress state and to describe the localization of the connected hydrogen resulting in the destruction of a material such localization places.

We suggest a novel approach to modeling the solids with account for the influence of hydrogen on the properties of free surface on monocrystals of various scales.

Application of two-continuum models to describing multiscale materials allows obtaining adequate results which describe SMART-influence on properties of these structures. In contrast to the homogeneous materials, the nanocrystal materials in the presence of hydrogen demonstrate stabilization of their properties as hydrogen decreases the surface energy of crystals in material and prevent their increasing up to the microsize.

## Acknowledgements

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