



Diffusion and release of hydrogen from metals under the effect of ionizing radiation



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ABSTRACT

The phenomenological model of non-equilibrium diffusion and release of hydrogen from metals under the effect of electron beam in the sub-threshold region is considered. It is shown that the radiation stimulates the release and diffusion of hydrogen at a rate, significantly exceeds the rate of thermal equilibrium processes in the metals. This can occur in the presence of long-lived, in a time scale of single phonon and electron relaxation, vibrationally excited H-bonds. The proposed model confirms the experimental results previously obtained.

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1. Introduction

Behavior of hydrogen in metals is an important technical and scientific challenge for a wide range of problems of fundamental and applied nature. The interest in the question of hydrogen permeability and accumulation is associated to the need for choosing the a constructive materials and solving the problems of materials science for the: fission and fusion reactor; plasma-chemical installations with hydrogen atmosphere; hydrogen accumulators in hydrogen energy; oil- and gas pipelines, etc. [1–4]. Hydrogen, dissolves in metals during melting, casting, at electro-chemical, and nuclear and other processes is one of the causes of defects, and cracks, which changes in the plastic properties of metals (hydrogen embrittlement), leading to a destruction of the products. Besides, metals and alloys have a unique property of accumulating and storing large amounts of hydrogen per unit volume, which is actually important in the problems of hydrogen energy [5]. Studying the mechanism of hydrogen embrittlement is a scientific problem, seeks to address the fundamental problem of

the negative influence of hydrogen on the mechanical properties of materials and to provide methods for the recovery of their properties, including during radiation exposure [6–8].

At the same time, Hydrogen, which is considered as the lightest atom and has a with high mobility in solids, is of independent interesting for studying its behavior in metals exposed to radiation. The migration of hydrogen from metals and alloys stimulated by radiation has been studied in connection with the problem of hydrogen embrittlement of the construction materials in fission and fusion reactors [7,8]. These studies have well-defined practical orientation and refer to conditions close to operational, neutron irradiation, γ -rays, protons and α -particles with energies above the threshold value, which forms defects in solids. Studies have shown that there is an increase in the diffusion rate and of hydrogen permeability in metals [7–11].

Interesting theoretical problems associated to the detection of hydrogen atmosphere in solids, are supplies to the ability to store the energy in solids, at a time much longer than the time of photon-electron relaxation in metals. Experimentally, it is shown that the process of diffusion and release of hydrogen from metals can be accelerated due to several effects, amongst irradiation and deformation [12,13].

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An excitation of vibrational degrees of freedom in the hydrogen subsystem takes place, under the effect of radiation energy. The diffusion of atoms in the presence of an excited subsystem of light atoms, can be stimulated not only by thermal vibrations energy kT , but also by the energy of non-equilibrium fluctuations of internal hydrogen atmosphere $\hbar\omega$, which in the conditions of feeding radiation can greatly exceed kT . The vibration-vibration exchange can effectively implemented in a hydrogen subsystem between the impurity states and the hydrogen subsystem. Under these conditions, the diffused hydrogen and impurities become non-equilibrium process, stimulated by the presence of excited hydrogen atmosphere. In contrast to electron, hydrogen-metal subsystem is able to maintain energy supply at a time, sufficient for the implementation of the accelerated diffusion processes.

2. Mechanisms of hydrogen migration under the effect of ionizing radiation

The existence of hydrogen in metals with concentration ($\geq 10^{19} \text{ cm}^{-3}$), saturates the broken bonds, capture the point defects, dislocations and micro-cavity. The irradiation under the effect of ionizing radiation with energy below the threshold value for defects formation causes: liberation of the hydrogen atoms of the dislocation [14,15], stimulated desorption of hydrogen from the grain boundaries [16] and non-equilibrium dissociation of hydrogen molecules in the micro cavities [16,17]. Hydrogen atoms in metals have extremely high mobility up to 10^{12} hops per second at temperature ($T = 300 \text{ K}$), which is 15–20 times higher than the mobility of heavy impurities at the same temperature [18]. In addition, under the effect of irradiation the local vibration of H-bonds lies outside the phonon spectrum of the crystal and in the process of forced relaxation, generated immediately 3–5 phonons or energy transferred by mechanism of “dipole (quadrupole) - charge” to electronic subsystem of solids. The speed of these processes is 10^7 – 10^{10} s^{-1} , and the H-bond vibrations are able to make about 10^5 – 10^6 oscillations before relaxation [19]. This form of the hydrogen subsystem produces favorable conditions for the exchange of vibration-translation (V - T exchange), non-equilibrium redistribution and release of hydrogen from the solid material by irradiation. Consequently, even in metals with fast relaxation in the electronic subsystem ($\tau \leq 10^{-13}$ – 10^{-14} s), the presence of light hydrogen atoms creates a condition of temporary accumulation of energy and contributes to the movement of hydrogen, and other impurity atoms. The electronic states of core atoms are excited by primary radiation provide the transfer of primary beam energy to the vibrational degrees of freedom of the internal H-subsystems. Under these conditions, the removal of hydrogen from the places of localization becomes thermally non-equilibrium and can't be stimulated by the energy of the thermal phonons kT , while it can be stimulated by long-lived non-equilibrium energy of vibrational excitation $\hbar\omega$ hydrogen subsystem.

The non-equilibrium energy of vibrational excitation of the hydrogen-metal subsystem can be estimated by comparing equilibrium and non-equilibrium diffusion coefficient of hydrogen.

For example, by irradiation of Pd samples with electrons at a temperature 40°C , the diffusion rate of hydrogen isotopes can be increased up to 30 times [20]. At the non-equilibrium internal excitation, the effective diffusion coefficient of the hydrogen subsystem given as [20]:

$$D^{ef} = \frac{\Gamma_{ex}}{\Gamma + \Gamma_{ex}} D_0 \exp\left(-\frac{E_D}{\hbar\omega}\right),$$

and for equilibrium internal excitation, the effective diffusion coefficient given as:

$$D = D_0 \exp\left(-\frac{E_D}{kT}\right),$$

Where Γ_{ex} – the generation rate of vibrational excited states in the hydrogen-metal subsystem; Γ – the relaxation rate of the vibrational excited states in metals, ($\Gamma/\Gamma_{ex} \cong 50$); E_D – activation energy of diffusion (0.23 eV for H in Pd [18]), the energy of the vibrational states can be estimated, as $\hbar\omega = 0.2 \text{ eV}$.

The relation between the equilibrium and the non-equilibrium effective diffusion coefficients at 313 K given as [20]:

$$\frac{D^{ef}}{D} = 30,$$

The close meaning of the energy can be obtained by estimation of the hydrogen plasma vibration energy (existing in palladium in form of protons) subsystem, if it is considered by the analogy of free electrons in metals.

If we consider that, the degree of saturation of Pd with hydrogen is high, and approximately one atom of H(D) for each atom of Pd, then energy of plasma vibration:

$$\hbar\omega = \hbar e \sqrt{\frac{\rho_{Pd} N_A}{\mu_{Pd} m_p \epsilon_0}} \cong 0.2 \text{ eV},$$

Where ρ_{Pd} , μ_{Pd} – the density and molar mass of palladium; m_p – the mass of proton; N_A – Avogadro's number; ϵ_0 – electric constant.

In this way, the degree of non-equilibrium ($\hbar\omega/kT$) and the life time of the excited hydrogen subsystem in metals may be high and sufficient to stimulate non-equilibrium diffusion and release of hydrogen and deuterium from metals by irradiation.

Another additional reason for the non-equilibrium emission of hydrogen (deuterium) from metal, saturated with H and D atoms, by irradiation is effectively reduced the potential barrier to release H^+ and D^+ from the depth of the metal to the surface. And also, neutralize them, and accelerate the recombination of H and D atoms to form the non-equilibrium desorption of molecules.

At a sufficiently high concentration of H(D)-bonds in the depth of metal, a vibrational excitation from the place of their generation begins to “propagate” throughout the entire volume of the sample as a result of resonance exchange of vibrational energy between the H-bonds, located in equivalent positions (Fig. 1 shows only the deuterium atoms, although we mean that by migration of H to the surface, they recombined to form H_2 , HD, and D_2 molecules). Since the oscillation frequency ω of light atoms H(D) are out side the phonon spectrum of the crystal, so the relaxation of these bonds by the phonon mechanism is complicated, and the hydrogen-metal subsystem moves under the effect of radiation energy in non-equilibrium vibrational excited state with energy $\hbar\omega$, more than the thermal energy kT .

When the energy of vibration excitation (H-L)^V connection exceeds the activation barrier of the transition path between two equivalent states in the lattice, a non-equilibrium migration of hydrogen from the depth of the metal started. The release of hydrogen from the volume of the metal, must overcome the surface potential barrier, associated with changes in the dimension of the system and electron capture. This potential barrier may be significantly reduced at the place of effect of the electrons beam on the specimen, where the neutralization process takes place in the conditions of equilibrium disturbance, also the migration to the surface is accelerated by the excitation of hydrogen subsystem (Fig. 1). The atoms of H(D) migrate to the metal surface and upon collision, these atoms recombined to form H_2 (D_2 , HD) molecules. The processes of migration of atoms to the surface and desorption of molecules are accelerated in the presence of vibration excitation

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