====== **STRENGTH** ======
AND PLASTICITY

Dislocation Slip in Hydrogenated Metals

V. V. Malashenko[1,2]

[1] *Donetsk National Technical University, ul. Artema 58, Donetsk, 83000 Ukraine*
[2] *Galkin Physicotechnical Institute, National Academy of Sciences of Ukraine,*
ul. Rozy Lyuksemburg 72, Donetsk, 83114 Ukraine

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Abstract—Dynamic drag force for edge and screw dislocations in metals, which is caused by their elastic interaction with hydrogen atoms, has been investigated. The drag force for an edge dislocation due to hydrogen atoms is shown to be a nonmonotonic function of the velocity with a pronounced maximum. In the case of screw dislocations, the drag force is considerably smaller in magnitude, has no maximum, and in the range of collective interaction is independent of the hydrogen concentration. Based on a comparison of different drag mechanisms, the concentrations and temperatures at which the velocity of dislocation slip is determined by the elastic interaction of the dislocation with hydrogen atoms have been determined.

INTRODUCTION

Studying mechanisms of interaction of hydrogen atoms with structural imperfections of the crystal lattice is an important problem of the theory of metals whose solution is essential to the understanding of the nature of the hydrogen effect on the properties of metals and alloys [1–4]. Numerous investigations give conclusive evidence of the existence of a close association of hydrogen embrittlement of metals with defects of the crystal lattice. The presence of hydrogen in metals may lead to both negative (for example, hydrogen "poisoning" of metals [5]) and positive (plasticizing of metals [6, 7]) consequences. In this connection, a problem of the effect of hydrogen atoms on the mobility of dislocations, whose motion brings about plastic deformation of crystals, is of very high priority.

The specific features of the behavior of hydrogen in metals are determined by its high solubility and great mobility [3]. Hydrogen atoms form atmospheres around dislocations, thereby producing additional drag upon dislocation slip. This dissipation mechanism was studied in detail in [8–10]. The mechanisms of drag for fast and slow dislocations are known to differ fundamentally [11]. The dislocation motion in crystals involves motion through various barriers related to lattice defects. The slowly moving dislocations overcome barriers due to thermal fluctuations. As the velocity of dislocations increases, their kinetic energy reaches the height of the energy barriers and the possibility of dynamic overcoming of the barriers arises. The range of dynamic drag of dislocations usually begins at velocities $v \geq 10^{-2}c$, where c is the velocity of propagation of transverse acoustic waves. In this case, as follows from [8–10], dislocations break away from their atmospheres. Since the velocity of dynamic slip of dislocations markedly exceeds the velocity of motion of hydrogen atoms, the latter atoms can be considered as immobile. Another feature of hydrogen—its high solubility in metals (especially, in Pd, Ta, Nb, and V)—is, on the contrary, very significant, since makes it possible to ensure the dominant influence of hydrogen atoms on the velocity of dislocation slip and, hence, on the rate of plastic deformation in the dynamic range.

The purpose of this work is to study dynamic drag for dislocations by hydrogen atoms. The mechanism of the energy dissipation in this case includes an irreversible conversion of the kinetic energy of a moving dislocation into the energy of dislocation vibrations excited by the elastic interaction of the dislocation with hydrogen atoms. Earlier, this mechanism of dislocation drag has not been investigated in hydrogenated metals.

RESULTS AND DISCUSSION

Consider an edge dislocation that moves under the action of a constant external stress σ_0 in a metal containing hydrogen atoms. Let the *OZ* axis be parallel to the dislocation line and its Burgers vector be parallel to the *OX* axis in the positive direction of which the dislocation slips with a constant velocity of *v*. The dislocation may execute small vibrations in the slip plane *XOZ*. Let us consider a hydrogen atom as a defect of the dilatation-center type. Indeed, in the case of transition metals, hydrogen atoms are predominantly located in tetrahedral positions [1]. The corresponding size of pores for metals with a bcc lattice is $r_1 = 0.29R$, where R is the radius of the solvent atom. At $R = 1.56$ Å (tungsten), $r_1 = 0.45$ Å, while the radius of a hydrogen atom is $r_H = 0.50$ Å. Consequently, upon arrangement of hydrogen atom in such a metal, a change in the crystal volume δV arises because of a misfit between the tetrapore size and the radius of hydrogen atom, and an energy of elastic interaction with a stress field of the edge dislocation appears. The quantity δV can be expressed in terms of

the partial volume of hydrogen atoms $\overline{V}$ (see [1]), i.e., $\delta V = \overline{V}/N_A$, where N_A is Avogadro's number.

The dislocation position is determined by the function $S(z, t) = vt + w(z, t)$, where $w(z, t)$ is the random function whose average value over an ensemble of defects and disposition of dislocation elements is equal to zero.

The equation of dislocation motion has the following form [12]:

$$m\frac{\partial S^2(z, t)}{\partial t^2} + \gamma\frac{\partial S(z, t)}{\partial t} - T\frac{\partial^2 S(zt)}{\partial z^2}$$

$$= b[\sigma_0 + \sigma_{xy}(vt + w; z)]. \tag{1}$$

Here, T is the coefficient of linear tension of the dislocation; the order of magnitude of the coefficient γ is determined by the expression $\gamma \approx B_0/m$, where B_0 is the coefficient of dynamic drag of the dislocation; and m is the mass per unit length of the dislocation whose value is determined by the expression

$$m = \frac{\rho b^2}{4\pi(1 - v)}\ln\frac{L}{r_0}, \tag{2}$$

where ρ is the crystal density, L is the quantity on the order of the dislocation length, b is its Burgers vector, and r_0 is the quantity on the order of atomic distances ($r_0 \approx b$). The characteristic value of the mass of a unit segment is on the order of 10^{-16} kg/m. The mass of a screw dislocation and that of an edge dislocation are on the same order. As was shown in [13], the effect of the constant B_0 on the drag force generated by a field of randomly distributed defects is small to the extent of the smallness of the dimensionless parameter $\alpha = \gamma\lambda v/c^2$, where λ is the cutoff parameter ($\lambda \approx b$). Since $B \leq 10^{-4}$ kg m^{-1} s^{-1} on the order of magnitude and the linear density of the dislocation mass is $m \approx 10^{-16}$ kg/m, we have $\gamma \leq 10^{12}$ s^{-1}. For the typical values $\lambda \approx b \approx 3 \times 10^{-10}$ m, $c \approx 3 \times 10^3$ m/s, and $v \leq 10^{-1}$ s, we obtain that $\alpha \ll 1$. For this reason, when calculating the force of dislocation drag by defects, we neglect the effect of the coefficient B_0 and leave in Eq. (1) the vanishingly small coefficient γ only to ensure the convergence of integrals appearing in the calculations.

The term σ_{xy} on the right-hand side of Eq. (1) is the component of the stress tensor generated by hydrogen atoms at the dislocation line, i.e., $\sigma_{xy} = \sum_{i=1}^{N}\sigma_{xy,i}$, where $\sigma_{xy,i}$ is the component of the stress tensor produced by an ith defect and N is the number of hydrogen atoms in the metal. Considering hydrogen atom as a defect of the dilatation-center type, the stress tensor produced by this defect can be written as

$$\sigma_{ik} = \mu r_H^3 \varepsilon\frac{\partial^2}{\partial x_i \partial x_k}\frac{1}{r}, \tag{3}$$

where μ is the shear modulus and ε is the misfit parameter of hydrogen atom.

In the second-order perturbation theory, the drag force of an edge dislocation can be determined by the formula (see [12])

$$F = b\left\langle\frac{\partial\sigma_{xy}}{\partial S}G\sigma_{xy}\right\rangle, \tag{4}$$

where G is the Green's tensor of Eq. (1) and the symbol $\langle...\rangle$ denotes the averaging over an ensemble of randomly distributed hydrogen atoms and over the dislocation length

$$\langle...\rangle = \lim_{L \to \infty}\int_{-L/2}^{L/2}\frac{dz}{L}\int_V\prod_{i=1}^{N}\frac{dr_i}{V^N}. \tag{5}$$

After required calculations, we obtain the expression for the drag force of the dislocation in the form

$$F = \frac{nb^2}{8\pi^2 m}\int d^3p|p_x||\sigma_{xy}(p)|^2\delta(p_x^2 v^2 - \omega^2(p_z)), \tag{6}$$

where integration is performed over the entire momentum space, n is the concentration of hydrogen atoms, $\delta(p_x^2 v^2 - \omega^2(p_z))$ is the Dirac delta function, and $\omega(p_z) = \sqrt{\Delta^2 + c^2 p_z^2}$ is the dispersion relation for dislocation vibrations. The expression for the activation Δ we can obtain solving the following equation

$$\Delta^2 = \frac{nb^2}{8\pi^3 m^2}\int d^3p\frac{p_x^2|\sigma_{xy}(p)|^2}{\Delta^2 + c^2 p_z^2 - p_x^2 v^2}. \tag{7}$$

Depending on the velocity of dislocation slip, the dynamic interaction of defects with a dislocation may be both of collective character and of the character of independent collisions [12]. Let us denote the time of interaction of the dislocation with a hydrogen atom as $t_H \approx (r_H/v)$ and the time of propagation of a perturbation along the dislocation for a distance on the order of the average distance between defects as $t_d \approx (l/c)$, where $l \approx n^{-\frac{1}{3}}$. In the range of independent collisions ($v > v_0 = r_H\Delta$), an inequality $t_H < t_d$ is fulfilled, i.e., within the time of interaction with hydrogen atom the dislocation element experiences no influence of other hydrogen atoms. In this range, Eq. (7) has no solution, i.e., no activation component arises in the dispersion relation. In the range of collective interaction ($v < v_0$), the inverse inequality, $t_H > t_d$, is fulfilled, i.e., when the dislocation element interacts with hydrogen atom, it has time to "feel" the influence of other hydrogen atoms that have induced a perturbance of the dislocation con-

figuration. In this range, the activation component appearing in the dispersion relation is written as

$$\Delta_{ed} = \frac{c}{b}(n_0 \varepsilon^2)^{1/3}. \tag{8}$$

Here, n_0 is the dimensionless concentration of point defects, $n_0 = nr_H^3$. The force of drag for the dislocation by hydrogen atoms has the form

$$F = Bv\Phi(r_H\Delta/v); \quad B = \frac{\pi n_0 b^2 \mu^2 \varepsilon^2}{3mcr_H\Delta^2}; \tag{9}$$

$$\Phi(x) = x^2[1 + (6x^4 + 2x^2)\ln(1 + x^{-2}) - 6x^2].$$

Now, we investigate an asymptotic behavior of this function. In the velocity range where $v > v_0$, we obtain $\Phi(x) \approx x^2$. This is the range of independent collisions. The drag force in this range is inversely proportional to the velocity of the edge-dislocation slip

$$F = \frac{\pi n_0 r_H b^2 \mu^2 \varepsilon^2}{3mcv}. \tag{10}$$

In the range of collective interaction ($v < v_0$), we have $\Phi(x) \approx 1$, and the drag of the dislocation by hydrogen atoms acquires a quasi-viscous character, i.e., the drag force in this case is a linear function of the velocity of dislocation motion

$$F = Bv. \tag{11}$$

Making use of data reported in [1], we now numerically estimate the coefficient of the dynamic drag of an edge dislocation that is caused by its interaction with hydrogen atoms. Thus, for iron $\mu = 8.3 \times 10^{10}$ N/m^2 and $b = 2.48 \times 10^{-10}$ m. At the concentration of hydrogen atoms $n = 10^{27}$ m^{-3}, we obtain $B = 8 \times 10^{-5}$ kg/(m/s) and the critical-velocity value $v_0 \approx 10^{-2}c \approx 30$ m/s. In the case of ultimately high concentrations (in palladium the ratio of the number of hydrogen atoms to the number of matrix atoms may reach unity), the constant B can be greater by an order of magnitude.

Let us attempt now to answer the question whether the interaction of hydrogen atoms with an edge dislocation can make the main contribution to the drag coefficient, i.e., define the velocity of dislocation motion and, hence, the rate of plastic deformation of the metal, and under what conditions this may occur. To answer this question, we will perform a comparative analysis of contributions of different drag mechanisms to the damping constant B resorting to results of [8]. At temperatures $T < T_e = 25$ K, the main channel of energy dissipation by moving dislocation is the interaction with conduction electrons $B_{el} \approx 10^{-6}$ kg/(m s). At $T_e < T < T_s \approx 100$ K, the magnon mechanism of drag becomes dominant (in this temperature range the damping constant corresponding to it is $B_s \approx 10^{-5}$–10^{-6} kg/(m s). At $T_s < T < \Theta_C \sim 1000$ K (Θ_C is the Curie temperature), the

drag of dislocations is largely determined by phonon scattering mechanisms: $B_{ph} \approx \approx 10^{-4}$–$10^{-5}$ kg/(m/s). The above estimates show that with due regard for the interaction of hydrogen atoms with the dislocation the total drag coefficient may change markedly, especially at high hydrogen concentrations and low temperatures (note that the dissipation mechanism considered is temperature-independent). The contribution of this interaction is significant even at room temperatures and may become dominant at the temperatures $T < T_s$, at which the phonon channels of dissipation cease to be effective.

Let us now consider the interaction of hydrogen atoms with a moving screw dislocation, for which purpose we make use of results of [14, 15]. The motion of screw dislocations in a crystal is described by the equation analogous to Eq. (1) in which it is necessary to replace the component σ_{xy} of the tensor of stresses produced by hydrogen atom in the metal by the component σ_{zy}. Since this alters the symmetry of the problem, such a replacement leads to a substantial change in the final result. It is also necessary to perform an analogous replacement in Eq. (7). Solving this equation, we obtain the following expression for the activation component in the spectrum of dislocation vibrations:

$$\Delta_{scr} = \frac{c\varepsilon n_0^{1/2}}{r_H} \approx \frac{c}{L_s}, \tag{12}$$

where L_s is the average distance between hydrogen atoms in the slip plane. Thus, the spectral gap depends on the concentration in different ways: in the case of edge dislocations, the gap is proportional to the cube root of the concentration of hydrogen atoms, i.e., is determined by the average distance between hydrogen atoms in the bulk of the crystal; in the case of screw dislocations, the gap is proportional to the square root of the concentration, i.e., depends on the average distance between hydrogen atoms in the plane of dislocation slip; in the second case, the numerical value of the activation component for $n = 10^{27}$ m^{-3} proves to be an order of magnitude smaller than in the first case. For example, for iron the activation values in the spectrum of the edge dislocation is $\Delta_{ed} = 10^{11}$ s^{-1} and in the spectrum of the screw dislocation is $\Delta_{scr} = 10^{10}$ s^{-1}. The force of drag of a screw dislocation by hydrogen atoms likewise is much less than that of an edge dislocation. In the range of independent collisions, we obtain for a screw dislocation

$$F_{scr} = \frac{\pi}{3}nr_H^3\varepsilon^2\mu b\frac{v}{c}, \tag{13}$$

the ratio of these forces is equal to

$$\frac{F_{scr}}{F_{ed}} = \frac{v^2}{c^2} \ll 1. \tag{14}$$

In the range of collective interaction, the drag force acting on a screw dislocation is determined by the expression

$$F_{scr} = \mu b \frac{v^3}{c^3}, \qquad (15)$$

while the ratio of the drag forces proves to be even smaller

$$\frac{F_{scr}}{F_{ed}} = (n r_H^3 \varepsilon^2)^{-1/3} \frac{v^2}{c^2} \ll 1, \qquad (16)$$

In the range of collective interaction, as follows from formula (15), the force of drag of a screw dislocation by hydrogen atoms is independent of both their concentration and the misfit parameter.

The critical velocity v_0 at which the character of interaction of a screw dislocation with hydrogen atoms changes is determined by the expression

$$v_0 = \varepsilon n_0^{1/2} c. \qquad (17)$$

For a screw dislocation in iron at the concentration of hydrogen atoms $n = 10^{27}$ m^{-3}, the critical velocity is $v_0 \approx 10^{-3}$ s, i.e., an order of magnitude smaller than that for an edge dislocation at the same hydrogen concentration.

Numerical estimates show that at $n = 10^{27}$ m^{-3} the damping constant caused by the interaction of a screw dislocation with hydrogen atoms is equal to $B_{scr} \approx 10^{-6}$ kg/(m/s), i.e., for this concentration the drag mechanism under consideration can play an important role only at $T < T_e$.

Since the rate of plastic deformation is proportional to the average velocity of dislocation slip, it may be concluded that under certain conditions the elastic interaction of hydrogen atoms with dislocations can exert an appreciable and even dominant effect on the rate of plastic deformation.

REFERENCES

1. N. M. Vlasov and V. A. Zaznoba, "Effect of Hydrogen Atoms on the Mobility of Edge Dislocations," Fiz. Tverd. Tela **41** (3), 451–453 (1999).

2. V. G. Bar'yakhtar, E. V. Zarochentsev, and V. V. Kolesnikov, "Effect of Hydrogen on Compression Moduli of 3*d* Transition Metals," Fiz. Tverd. Tela **32** (8), 2449–2455 (1990).

3. *Hydrogen in Metals*, Ed. by G. Alefeld and J. Völkl (Springer, Berlin, 1978; Mir, Moscow, 1981).

4. M. P. Peshcherenko, V. V. Rusakov, and Yu. L. Raikher, "A Model of the Deformation Behavior of Hydrogenated Group V Metals," Fiz. Met. Metalloved. **97** (4), 17–27 (2004) [Phys. Met. Metallogr. **97**, 342–351 (2004)].

5. B. A. Kolachev, *Hydrogen Brittleness of Metals* (Metallurgiya, Moscow, 1985) [in Russian].

6. V. K. Nosov and B. A. Kolachev, *Hydrogen Plasticization upon Hot Deformation of Titanium Alloys* (Metallurgiya, Moscow, 1986) [in Russian].

7. D. N. Karpinski and S. V. Sannikov, "Analysis of the Plasticizing Effect of Hydrogen Dissolved in a Crystal on the Evolution of Plastic Deformation at the Tip of a Crack," Fiz. Tverd. Tela **42** (12) (2000) [Phys. Solid State **42**, 2236–2240 (2000)].

8. A. H. Kottrel, *Dislocations and Plastic Flow in Crystals* (Oxford University Press, Oxford, 1953; Metallurgiya, Moscow, 1958).

9. H. Yoshinaga and S. Morozumi, "The Solute Atmosphere Round a Moving Dislocation and Its Dragging Stress," Philos. Mag. **23** (186), 1367–1385 (1971).

10. B. S. Altundzhi and B. Ya. Lyubov, "Distribution of Impurity Atoms around a Moving Dislocation," Fiz. Tverd. Tela **15** (3), 755–761 (1973).

11. V. I. Al'shits and V. L. Indenbom, "Dynamic Drag of Dislocations," Usp. Fiz. Nauk **115** (1), 3–39 (1975).

12. V. V. Malashenko, V. L. Sobolev, and B. I. Khudik, "Self-Consistent Description of the Effect of Point Defects on Spectrum and Dynamic Deceleration of Dislocations," Phys. Status Solidi B **143** (2), 425–431 (1987).

13. V. D. Natsik and K. A. Shishko, "Effect of Impurities on Dynamic Dragging of Dislocations," Cryst. Res. Technol. **19** (6), 763–768 (1984).

14. V. V. Malashenko, "Dynamic Drag of Screw Dislocation by Point Defects," Fiz. Tverd. Tela **32** (2), 645–647 (1990).

15. V. V. Malashenko, "The Interaction between an Ensemble of Point Defects and a Moving Screw Dislocation," Fiz. Tverd. Tela **39** (3), 493–494 (1997).