



HYDROGEN-INDUCED COLD CRACKS IN WELDED JOINTS OF HIGH-STRENGTH LOW-ALLOYED STEELS (Review)

I.K. POKHODNYA, A.V. IGNATENKO, A.P. PALTSEVICH and V.S. SINYUK

E.O. Paton Electric Welding Institute, NASU

11 Bozhenko Str., 03680, Kiev, Ukraine. E-mail: office@paton.kiev.ua

Possibility of development of hydrogen-induced cold cracks in welded joint depends on series of interconnected and complex physical phenomena. Work represents a short review of investigations carried out in the E.O. Paton Electric Welding Institute on study of processes of hydrogen absorption by metal, its diffusion in the welded joint considering kinetics of temperature gradient, hydrogen traps and residual stresses. Peculiarities of hydrogen diffusion in strain-free and plastically deformed metal were studied by experiment-calculated methods. Results of experiment-calculation investigations and mathematical modeling of mechanisms of generation and growth of hydrogen-induced cracks in welded joints on micro- and macrolevel are stated. It is shown with high reliability that interaction of hydrogen with dislocations makes the basis of mechanism of hydrogen embrittlement. Hydrogen influences nucleation and growth of microcracks in metal making coalescence of dislocations easier that result in localizing of plastic strain under effect of hydrogen. As it is showed by computer modelling of development of microdefects in metal, the reduction of grain size, at other factors being equal, increases metal sensitivity to negative influence of hydrogen. Mechanism of crack growth in metal containing hydrogen is proposed considering effect of hydrogen-enhanced localized plasticity. 64 Ref., 12 Figures.

Keywords: *brittle fracture, hydrogen embrittlement model, hydrogen-enhanced localized plasticity, residual stresses, BCC metals, grain size, hydrogen diffusion*

Steel is one the most effective structural materials. More than 20 bln t of steel are used in different parts and structures in present time. 1550 mln t of steel were manufactured in the world in 2012, and in further 40 years volume of production would hypothetically increase by 50–100 % [1]. At that welding remains one of the most widespread methods for obtaining of permanent metal joints. As far as the requirements to strength of source materials and quality of obtained joints constantly rise in a course of time, it could be supposed that problems existing in development of more safe and long-term welded joints would be relevant and economic importance of scientific investigations directed on solution of given problems would permanently increase.

High-strength low-alloyed (HSLA) steels due to increasing requirements to service characteristics of welded structures are used in machine building, construction engineering, shipbuilding and pipeline construction. There is a risk of appearance of cold cracks in zone of welded joint in welding of HSLA steels. It was determined that one of the main factors promoting formation

of cold cracks is hydrogen absorbed by liquid metal from arc plasma. The results of carried out experimental and theoretical investigations show that hydrogen-induced cold cracks (HICC) are the consequence of more general physical effect, i.e. hydrogen embrittlement (HE) under specific conditions of thermal-deformation welding cycle [2].

Possibility of development of HICC in the welded joint depends on series of interconnected and complex physical phenomena. For their study the processes of hydrogen absorption by metal, diffusion of hydrogen in welded joint allowing for kinetics of temperature gradient, hydrogen traps and residual stresses were investigated as well as mathematical modeling of mechanisms of formation and growth of HICC on micro- and macrolevel was performed, and experiment-calculated investigations of mechanisms of HICC formation in welded joints were carried out at the E.O. Paton Electric Welding Institute.

Forms of hydrogen in iron and steels. Characteristics and state of hydrogen in metal volume are to be known for deep understanding of HE mechanism. Experimentally stated that process of hydrogen dissolution in iron follows the Siverts' law, i.e. under thermodynamic equilibrium a concentration of dissolved hydrogen is directly proportional to square root of value of



its pressure in gas phase. This means that hydrogen like other biatomic gases is absorbed in form of atoms.

In spite of the fact that atomic hydrogen is the simplest substance soluble in iron, corresponding methods of calculation of its state based on different theories have not yet been developed. It is assumed that dissolved hydrogen can be in several forms, i.e. protonic, anionic and atomic. Occurrence of metallic bonding characterizing by sharing of valence electrons of iron and hydrogen electron takes place between atoms in metal during formation of protonic form. However, experimental observations of directed movement of hydrogen under effect of electric field do not provide precise answer to question about charge state of hydrogen in metal [3, 4]. The effect of transfer will be determined by particle charge [3] only in absence of interaction between the particles of migrating component and charge carrier in metal.

Quantum mechanical calculations were used for analyzing of possibility of existence of different forms of charge state of hydrogen depending on parameters of electron interaction in «hydrogen-metal» system [5]. It was concluded based on obtained results that protons H^+ , neutral atoms H^0 and negative ions H^- can be present in metal simultaneously with different possibilities. In authors' opinion, the main question lies in the fact in what condition the hydrogen will have the maximum effect on physico-mechanical properties. In V.I. Shvacko opinion [6] this conclusion causes doubts on alternative problem formulation about charge state of hydrogen in metal, but does not clear the situation itself. Conclusion about necessity to concentrate on determination of the most active form of hydrogen virtually means return to initial statement of problem since problem about charge state of hydrogen has appeared exactly from the necessity of determination of mechanism of its abnormal effect on metal properties.

Calculating electron structure of iron-hydrogen FCC system, the authors [7] came to the conclusion that density of valence electrons increases near hydrogen atom, i.e. negative charge is concentrated around hydrogen atoms. Calculations also showed from point of view of electron theory of metals that density of free electrons around the atoms of hydrogen being present in dislocations increases as well. This results in increase of dislocation mobility and reduction of distance between them in dislocation cluster [8].

It was shown using method of secondary ionic emission that hydrogen diffusing from metal

depth has negatively charged state on the surface [9, 10].

Model, according to which atoms of hydrogen introduced in metal lattice are localized in void of that or another type and make oscillatory motions near equilibrium position in accordance to atomic structure of solid solution, obtained wide distribution in authors' opinion [11]. Potential holes for atoms of hydrogen located in quasi equilibrium conditions are sufficiently deep (against their average kinetics energy). Such a model, apparently, describes the most significant peculiarities of the solution, i.e. in such form it provides the possibility accurately, by order of magnitude, calculate diffusion coefficients and explain the reasons of their exponential dependence on temperature, that is approved by direct experiments.

Hydrogen absorption. Processes of absorption of gases by electrode metal and weld pool develop significantly in welding of steels under conditions of high temperatures of arc discharge and high rates of heating and cooling of metal. Increase of hydrogen concentration in metal rises a risk of initiation of cold cracks in welded joint and, as a result, failure of whole welded structure [2, 12]. Thus, one of the main solutions of problem of HICC prevention is a fundamental investigation of hydrogen behavior in welding, searching of ways of reduction of its content in the weld metal and development of new welding consumables based on obtained results.

Content of H_2 and H_2O in arc atmosphere, metal temperature, presence of layer of slag and its properties, kinetics of electrode melting and transfer of electrode metal in the weld pool are mainly used for determination of hydrogen absorption by molten metal. High partial pressure of molecular and atomic hydrogen in arc gap as well as temperature of liquid metal at the end of electrode and weld pool provide for intensive hydrogen absorption. Experimentally showed that high rate of cooling of drops of electrode metal allows registering high contents of hydrogen [13].

Performance of experimental investigations on interaction of hydrogen with metal at the end of electrode and weld pool under conditions of arc welding is significantly complicated due to high temperatures, dissociation and ionized state of gases and, as a result, high reaction speeds [14–17]. Therefore, physical and mathematical models of processes, based on ideas about existence of local thermodynamic equilibrium in arc column, were developed and applied for investigation of processes of hydrogen absorption by



metal in arc welding. Mathematical model of process of hydrogen absorption by metal proposed in [14–16] is based on system of equations of gas dynamics and equation, which describes molecular interaction in thin Knudsen layer adjacent to metal surface, as well as equation of hydrogen mass transfer in metal. Evaporation of metal from drop surface was considered in calculation of absorption of hydrogen by drop of electrode metal. It is shown that reduction of arc temperature increases efficiency of hydrogen bonding by fluorine and oxygen. It was determined that effect of abnormal absorption of hydrogen by metal interacting with plasma of arc discharge is defined by degree of molecular dissociation in plasma volume, which depends on energy of molecular dissociation and temperature of plasma, and not by absorption of accelerated charged particles.

Maximum solubility in contact of iron with hydrogen under conditions of thermodynamic equilibrium is observed at $T = 2600$ K. Further increase of temperature results in reduction of hydrogen solubility caused by intensive iron evaporation. Calculation, proved by experiment, showed that absorption of hydrogen from plasma of arc discharge multiply exceeds (more than 10 times) absorption under equilibrium conditions at $T = 2000$ K, and is determined by degree of hydrogen dissociation depending on arc temperature. Also, monotonous reduction of content of hydrogen in iron is observed with increase of its temperature due to iron evaporation in contact with $\text{Ar} + \text{H}_2$ plasma.

Entering of fluorine compounds in composition of welding consumables is one of the most efficient methods of reduction of hydrogen absorption by liquid metal. Thermodynamic analysis of behavior of HF in arc zone was carried out in work [18]. HF and OH are completely dissociated in accordance with radial distribution of temperature in central high-temperature region at $T = 6200$ K. HF is not dissociated at column periphery (2500 K) that shows the possibility of hydrogen bonding by fluorine in arc zone.

Thermodynamic approach was also used for analysis of processes of bonding of hydrogen being in gas phase in a form of water vapors (at $P = 1 \cdot 10^5$ Pa pressure) by slags of $\text{TiO}_2\text{--CaO--CaF}_2$, $\text{Al}_2\text{O}_3\text{--CaO--CaF}_2$, $\text{SiO}_2\text{--CaO--CaF}_2$ system. It is shown that minimum content of hydrogen in metal is typical for $\text{TiO}_2\text{--CaO--CaF}_2$ and $\text{Al}_2\text{O}_3\text{--CaO--CaF}_2$ slag systems depending on CaO content in slag melt [19, 20]. In $\text{Al}_2\text{O}_3\text{--CaO--CaF}_2$ system weight fraction of CaO has no influence on hydrogen content in metal. Ad-

dition of SiF_4 in gas phase has effective influence on decrease of hydrogen content in metal due to reaction of HF formation and reduction of partial pressure of hydrogen.

Presence of mainly fluorosilicate compounds and anhydrous hydrogen fluoride was detected by mass-spectrometric investigations [21] of fluorides included in gases emitted from arc zone in welding by flux-cored wires which contain CaF_2 , SiO_2 , MgO , CaO , ZrO_2 . Composition of forming gases [22] was investigated in process of arc heating of CaF_2 specimen at $T = 147$ K. HF, which was formed at interaction of CaF_2 and residual vapors of water in mass spectrometer, was found in mass spectrum of gases in both experiments.

Accurate data on concentration of hydrogen in weld metal is necessary for development of efficient measures of reduction of hydrogen absorption by liquid metal, control of quality of welding consumables, prevention of formation of cold cracks and pores. Mercury method based on ISO 3690:2000(E) is a widely used method applying eudiometers. Developed method of analysis of diffusion hydrogen with chromatographic ending provides the possibility of measurement of volumes of hydrogen emitted from specimen with high accuracy and sensitivity, as well as allow accelerating measurement of quantity of hydrogen due to specimen heating 30–50 times. Chromatographic method is introduced in GOST 23338–91.

Investigations of effect technological factors of welding on hydrogen quantity in the weld metal [23, 24] were carried out using developed method. It is determined that changes of welding speed and value of welding current for coated electrodes do not virtually change concentration of hydrogen in the weld metal, but at the same time, content of hydrogen related to deposited metal significantly rises with increase of welding speed. Thus, a conclusion can be made that a content of hydrogen in molten weld metal is necessary to be determined for accurate estimation of diffusion hydrogen. Average concentration of hydrogen in multilayer deposited metal does not exceed content of hydrogen in single-run weld metal.

One of the main methods for reduction of hydrogen content in weld metal is preliminary heat treatment of welding consumables, at which part of hydrogen in a form of H_2O is removed. Allowable temperatures of baking for coated electrodes make 400–450 °C, and for flux-cored wires are 250–270 °C and they do not allow removing all moisture present in components of welding



consumables. Temperature dependence of removal of H_2O and H_2 (up to 1000 °C) from gas-slag-forming and alloying components was investigated using thermal desorption analysis [25] which allowed determining methods of their treatment for reduction of level of potential hydrogen in welding consumables. Application of heat-treated components in composition of the coated electrodes provided obtaining of extremely low concentrations of diffusion hydrogen (1.0–1.5 ml/100 g) in the weld metal [26].

Hydrogen diffusion. Redistribution of hydrogen in metal of the welded joint takes place after its absorption by weld pool. Field of hydrogen concentration in the joint is necessary to be known for determining the zones of metal of welded joint susceptible to the highest risk of HICC initiation. Thus, nonstationary problem of hydrogen diffusion considering thermal-deformation cycle of welding, structural transformations and hydrogen traps [2] is solved in a general case.

Moving force of diffusion is a gradient of chemical potential, the value of which depends on hydrogen solubility in metal, diffusion coefficient, gradients of concentration and temperature, stressed state and plastic deformations [27]. At that, thermal-deformation cycle of welding results in significant inhomogeneity of hydrogen concentration field.

Diffusion of hydrogen in the weld metal and redistribution of hydrogen in welded joint after welding were studied experimentally and using mathematic modelling. Experiments on kinetics of removal of hydrogen, being absorbed in process of welding, from cylinder specimens of the weld metal were carried out, and dependence of speed of degassing V on quantity of hydrogen Q in specimen $V(Q)$ were obtained for determination of value of effective coefficient of hydrogen diffusion D_H . D_H was determined based on obtained experimental dependence $V(Q)$ using solution of reverse coefficient isothermal problem. $D_H = 1 \cdot 10^{-7} \text{ cm}^2/\text{s}$ for metal welds performed using rutile welding consumables at $T = 20^\circ\text{C}$, and $D_H = 1 \cdot 10^{-6} \text{ cm}^2/\text{s}$ [28] was obtained for low-alloy killed welds.

Removal and redistribution of hydrogen in metal of welded joint take place after welding. Using results of experimental investigation [29] a mathematical model of redistribution of hydrogen between the weld metal and base metal [30] was developed, which allows determining current concentration of hydrogen in zones of welded

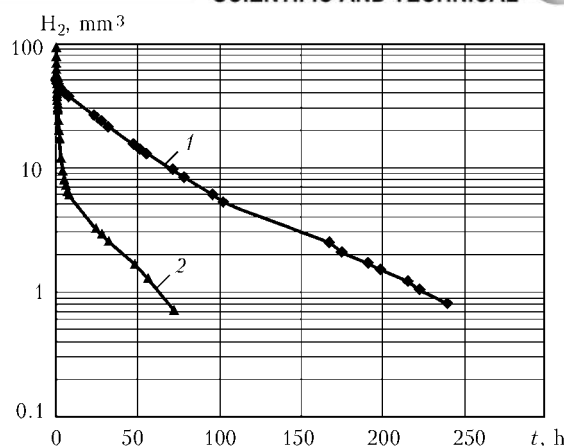


Figure 1. Results of experiments on kinetics of hydrogen removal from deformed (1) and undeformed (2) specimen

joint considering hydrogen absorption by defects of metal crystalline structure. Applied stresses significantly influence on D_H value and hydrogen permeability of steel at plastic strain [31].

Plastic strain in fracture zone precedes as a rule metal failure. Plastic strain of weld metal and HAZ is possible as a result of thermal-deformation cycle of welding or due to external loading. In this case, interaction of hydrogen with formed dislocation structure takes place. The dislocations are reversible traps, which at metal temperature lower than 100 °C start to provide significant effect on hydrogen diffusion. Besides, as follows below, basis of HE lies in interaction of hydrogen with mobile edge dislocations. Therefore, study of hydrogen diffusion in plastically deformed metal is of particular interest in scope of HE investigation.

Results of investigation of kinetics of hydrogen removal at room temperature are shown in Figure 1 [32]. Character of hydrogen diffusion in undeformed and plastically deformed metal has noticeable difference. As computer calculations based on experimental data showed, D_H remains constant in plastically deformed metal virtually during the whole degassing processes. Therefore, completely all hydrogen is bonded with dislocation structure to the moment of degassing beginning, and in order that hydrogen atom can move out from the metal it firstly needs to overcome energy barrier and detach from dislocation holding it. Respectively, D_H value in deformed metal is determined by average energy of bonding of hydrogen atoms with dislocations and does not change in the degassing processes.

According to calculations, D_H changes by several orders (Figure 2) in undeformed specimen in a process of dissociation. Only part of hydrogen is bonded with dislocation structure in the

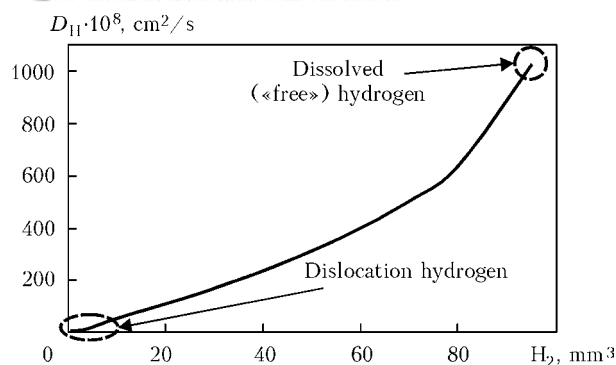


Figure 2. Calculation dependence of D_H on hydrogen content in metal

beginning of degassing in undeformed metal due to relatively small concentration of dislocations. Initially, when desorption of hydrogen not bonded with dislocations takes place, the dislocations have no significant effect on diffusion process and, respectively, on D_H value. But, as far as desorption takes place the portion of hydrogen, which was initially bonded with dislocation structure, increases in general flow of degassed gas. Thus, increase of time of degassing provides reduction of concentration of remained hydrogen, and rise of influence of dislocations on character of hydrogen diffusion in metal is observed. This leads to gradual reduction of D_H value and speed of specimen degassing. When hydrogen concentration is low, D_H value in undeformed metal is comparable with its value in deformed metal that confirms the conclusions about role of dislocation structure made before.

Work [33] proposes a mathematical model of hydrogen mass transfer in metal considering

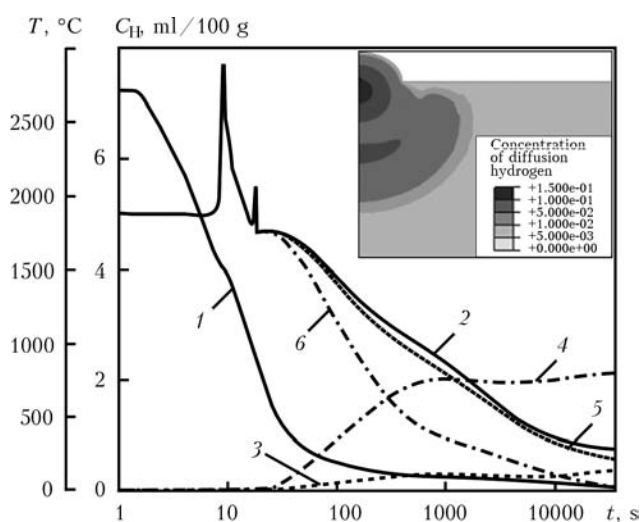


Figure 3. Dependence on time of temperature T (1) and hydrogen concentration C_H : 2 — diffusion (without traps); 3, 4 — in traps with $E_b = 20$ and 30 kJ/mol, respectively; 5, 6 — diffusion with $E_b = 20$ and 30 kJ/mol, respectively (concentration of diffusion hydrogen in 10 h after welding is shown in the right upper corner)

traps, which describes redistribution of hydrogen between residual and diffusion one. Dislocations formed as a result of structural transformations in metal during cooling were considered as traps. Calculation of mass transfer of hydrogen in welded joint was carried out by finite element method from moment of beginning of weld metal solidification (Figure 3).

Local concentration of hydrogen C_H in weld center in moment of its solidification as well as during structural transformations rapidly increases due to solubility jump (see Figure 3). Concentration of residual hydrogen (bonded with dislocations) increases with cooling of metal up to 100°C and depends on bond energy of traps with hydrogen E_b . Thus, at presence in metal of traps with $E_b = 20$ kJ/mol the quantity of residual hydrogen makes $0.5 \text{ cm}^3/100 \text{ g}$, and behavior of diffusion hydrogen does not significantly change.

In case of traps with $E_b = 30$ kJ/mol the quantity of residual hydrogen increases up to $2 \text{ cm}^3/100 \text{ g}$, and content of diffusion hydrogen rapidly reduces. After traps are saturated, significant delay of hydrogen diffusion takes place due to reduction of gradient of concentration of diffusion hydrogen as a result of its transfer in residual one. Thus, resulting reduction of local concentration of diffusion hydrogen in the weld center (in 10 h after welding) appears to be smaller than increase of residual one.

Hydrogen transfer by edge dislocations. Peculiarities of reversible hydrogen embrittlement (for example, temperature-speed dependence of metal sensitivity to hydrogen embrittlement) according to current representations are explained by interaction of hydrogen dissolved in metal with mobile edge dislocations [6, 34]. Mathematical model was proposed in [35] for description of process of hydrogen transfer by edge dislocations. Atom of hydrogen moving inside the metal as a result of interaction with lattice will have different potential energy in different moments of time. Possibility of transfer of interstitial atoms in specific adjacent void depends on metal temperature, potential energy of atom in initial and finite void. Based on concepts of microscopic theory of diffusion and considering that atom of hydrogen can jump in adjacent void only if it is not occupied by other atoms, the following system of equations describing diffusion of hydrogen in the field of mobile edge dislocation [36] can be obtained:



$$\begin{cases} j_x = -D \left[\frac{\partial u_D}{\partial x} p(1-p) + \frac{\partial p}{\partial x} \right] + V_0 p, \\ j_y = -D \left[\frac{\partial u_D}{\partial y} p(1-p) + \frac{\partial p}{\partial y} \right] + V_0 p, \\ \frac{\partial(j_x)}{\partial x} + \frac{\partial(j_y)}{\partial y} = 0, \end{cases}$$

where J_x and J_y are the flow of hydrogen along x and y axes, respectively; D is the coefficient of hydrogen diffusion in defect-free metal; u_D is the potential of interaction of hydrogen with edge dislocation; $p = C/C_v$ is the hydrogen concentration related to number of voids; C_v is the number of voids in volume unit; V_0 is the speed of movement of edge dislocation with conditions at infinity: $p = p_0 = C/C_v$; $J_x = V_0 C_0/C_v = V_0 p_0$; $J_y = 0$ at $(x^2 + y^2) \rightarrow \infty$.

Effect of metal temperature, speed of movement of edge dislocations and concentration of diffusion hydrogen on quantity of hydrogen transferred by dislocations was investigated. The calculations showed that dependence of quantity of hydrogen transported by edge dislocation N on temperature has maximum in field of room temperature (Figure 4). It is determined that increase of speed of edge dislocation movement or reduction of diffusion hydrogen concentration decreases quantity of transported hydrogen and maximum of $N(T)$ curve is shifted in area of higher temperatures [36]. Since movement of dislocation is an elementary act of plastic deformation then increase of speed of plastic deformation rises speed of dislocation movement. The results of calculation are well matched with experimental data, i.e. increase of speed of plastic deformation reduces metal sensitivity to HE, and minimum of brittle strength of specimens containing hydrogen is shifted in area of higher temperatures [12].

Mechanical investigations. Works [37–39] proposed new physically based criterion characterizing the degree of reduction of brittle strength of metal under effect of hydrogen, and procedure of its determination was developed on data of mechanical tests. In contrast to comparison criteria used earlier, new criterion has clear physical content determined by metal structure. Application of this procedure allows estimating the degree of metal HE by means of performance of the simplest uniaxial tensile tests of standard specimens.

Works [40–43] show that measure of brittle strength of metal is a value of microcleavage resistance R_{mce} , i.e. minimum stress of brittle frac-

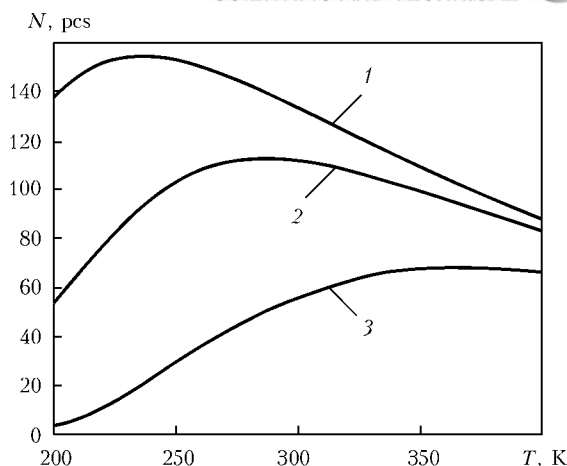


Figure 4. Dependence of hydrogen quantity N transported by section of mobile edge dislocation on temperature of specimen and speed of its movement $V_0 = 1 \cdot 10^{-3}$ (1), $1 \cdot 10^{-2}$ (2) and $1 \cdot 10^{-1}$ (3) m/s

ture at uniaxial tension deformed per certain degree e . Since R_{mce} value is structurally determined in relation to temperature, then change of R_{mce}^H/R_{mce} relation depending on temperature reflects influence of hydrogen on this value. Peculiarities of R_{mce} value marked in [40–43] allow expressing degree of reduction of brittle strength of metal under effect of hydrogen δ_H through decrease of value of critical fracture stress σ_{1C} in specimen waist:

$$\delta_H = \frac{R_{mce}^H}{R_{mce}} \approx \frac{\sigma_{1C}^H}{\sigma_{1C}},$$

where R_{mce}^H and σ_{1C}^H are the characteristics of metal containing hydrogen.

σ_{1C} for concerned temperature interval should be calculated based on data of mechanical tests for determination of δ_H parameter. Estimation of δ_H value is obtained after dividing at fixed e and $\sigma_{1C}^H/\sigma_{1C}$.

Results of experimental investigations of hydrogen effect on mechanism of metal fracture are given in work [44]. Thermodesorption analysis determined that residual hydrogen which is bonded with formed dislocations and microcracks (Figure 5) is generated in metal containing diffusion hydrogen as a result of plastic deformation. Thus, density of dislocations increases and microdefects are formed as a result of plastic deformation of metal that leads to hydrogen redistribution.

Specimens from VSt3sp (killed) steel containing $7 \text{ cm}^3/100 \text{ g}$ of hydrogen were stretched to different degrees of plastic deformation for studying of effect of hydrogen on mechanisms of nucleation and growth of microdefects in metal. After preliminary deformation the hydrogen was

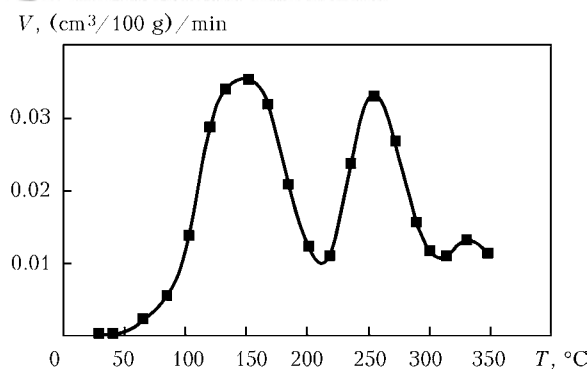


Figure 5. Spectrum of thermodesorption of residual hydrogen for VSt3sp steel specimen, containing $8.5 \text{ cm}^3/100 \text{ g}$ of diffusion hydrogen, after fracture

removed and specimens were stretched up to failure. The specimens containing no hydrogen were subjected to identical cycle of testing. Hydrogen provides no significant effect on mechanical properties of VSt3sp steel (Figure 6, *a*) up to 10 % deformation of specimen, and increase of deformation from 15 up to 17 % results in significant effect of hydrogen on metal failure (Figure 6, *b*, *c*). Brittle microcrack, the growth of which takes place on tough mechanism after hydrogen removal (Figure 6, *d*), was found on the fracture surface of specimens with $7 \text{ cm}^3/100 \text{ g}$ content of hydrogen and preliminary deformation.

Deformation of metal containing hydrogen results in nucleation and growth of microdefects in it that significantly influence mechanical properties. Effect of hydrogen rapidly increases in achieving of certain level of plastic deformation. Presence of hydrogen on dislocations facilitates their coalescence that results in microcrack nucleation at lower external stress.

Mechanism of hydrogen embrittlement of iron and steel. Formation of HICC in welded joints from HSLA steels are determined by peculiarities of structural transformations in weld metal and HAZ, value of residual tensile stresses and concentration of hydrogen in metal [9, 45]. Mechanism of more general physical phenomenon of degradation of mechanical properties of metal under effect of dissolved hydrogen, i.e. hydrogen embrittlement [9], is necessary to be considered for detection of mechanism of HICC formation under conditions of thermal-deformation cycle of welding.

Hydrogen at plastic strain is transported to place of crack nucleation by mobile dislocations. Dislocation theory proposes a number of models of dislocation reorganizations which can result in formation of extremely sharp nucleation sub-microcrack [46]. One of them is Zener–Stroh

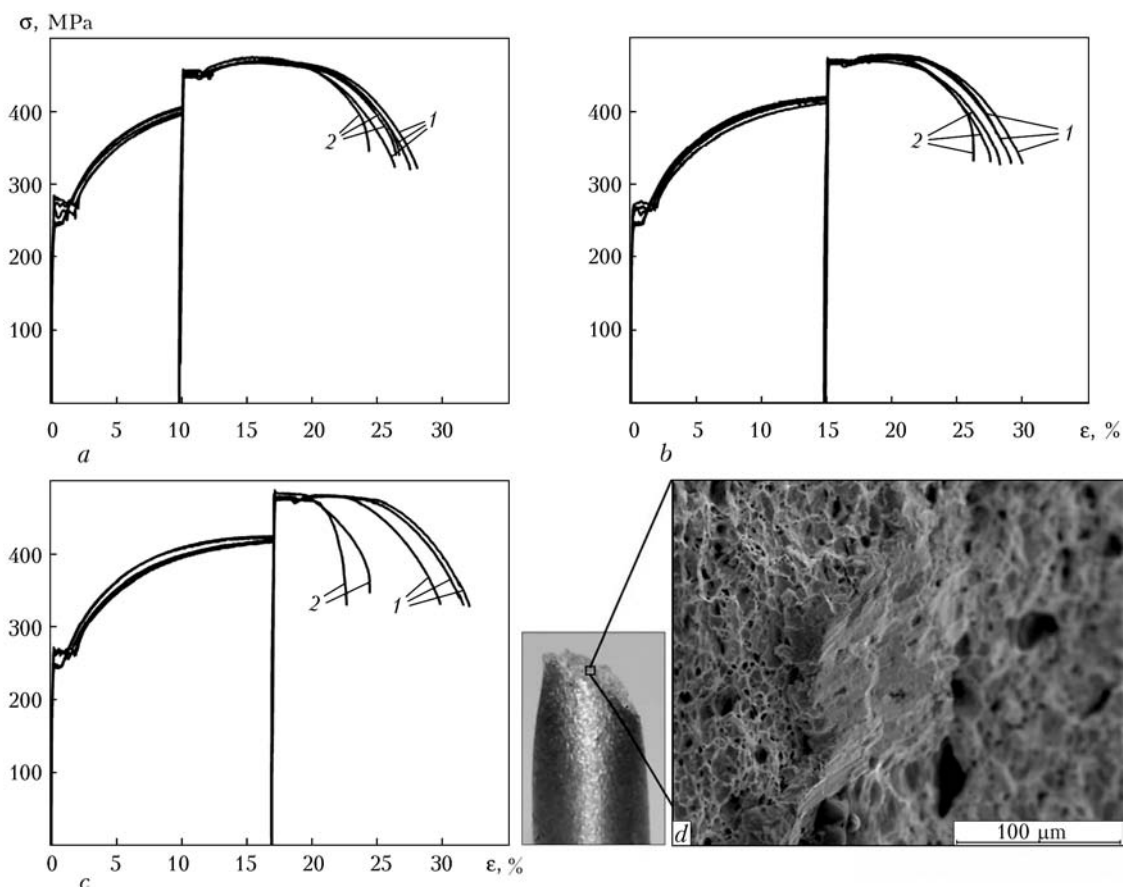


Figure 6. Tensile diagrams for VSt3sp steel specimens with preliminary deformation e_{pr} of 10 (*a*), 15 (*b*) and 17 (*c*) % (1, 2 – specimens containing no hydrogen and containing it respectively), and microstructure of microcrack (*d*)

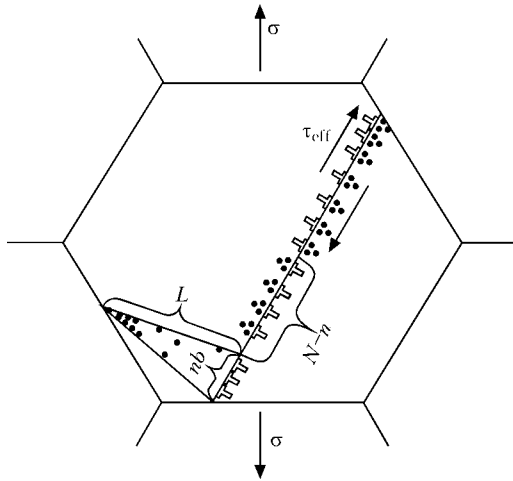


Figure 7. Scheme of microcrack formation: σ — external tensile stresses; τ_{eff} — tangential stresses acting in slide plane of dislocations; L — length of submicrocracks; N — total quantity of edge dislocations in plain cluster; n — quantity of dislocations merged in submicrocrack; b — modulus of Burgers vector

model, according to which cluster of dislocations is formed in a place of stop of slip band and occurrence of tensile stress takes place in its top, which under certain force conditions is developed in microcrack (Figure 7). Presence of hydrogen around the dislocations results in nucleation of submicrocrack at lower stress due to facilitation of dislocation coalescence.

If stability of microcrack is lost in a process of nucleation, then brittle fracture of metal will take place [47, 48]. If crack does not loose stability, then its further growth will depend on peculiarities of development of local plastic strain in zone around microcrack tip and hydrogen concentration [49, 50] (Figure 8).

Presence of hydrogen results in change of morphology of plastic area due to localized plastic strain [51–53]. New microdefect [54] (Figure 9) is nucleated in shear band near microcrack tip under hydrogen effect.

Change of character of microplastic strain around micropores or nonmetallic inclusions under effect of hydrogen promotes transfer from

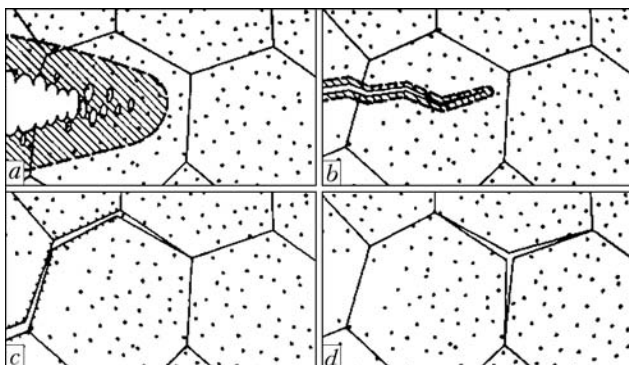


Figure 8. Mechanism of crack growth: *a* — tough; *b* — quasi-brittle; *c, d* — intergranular

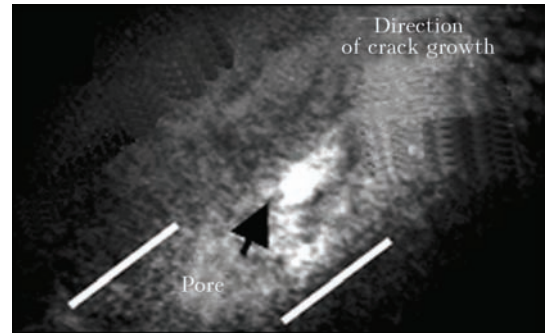


Figure 9. Formation of micropore in specimen from IN903 steel containing hydrogen [54]

tough to brittle fracture due to hydrogen-enhanced localized plastic strain [55, 56] (Figure 10).

Thus, critical factors on the stage of microcrack development are the main tensile stresses and quantity of hydrogen transferred by dislocations to the place of defect formation (determined by concentration of diffusion hydrogen, temperature, speed of deformation and dislocation density in metal). Mechanism of microcrack growth (tough or brittle), if it does not loose stability in the moment of its nucleation, is determined by stress intensity factor and hydrogen concentration in the crack tip.

Plastic strain of metal results in increase of number of mobile dislocations that, in turn, leads to redistribution of diffusion hydrogen between the lattice and reversible traps-dislocations. Hydrogen, transferred by dislocations to place of microcrack nucleation, will be molized inside the latter.

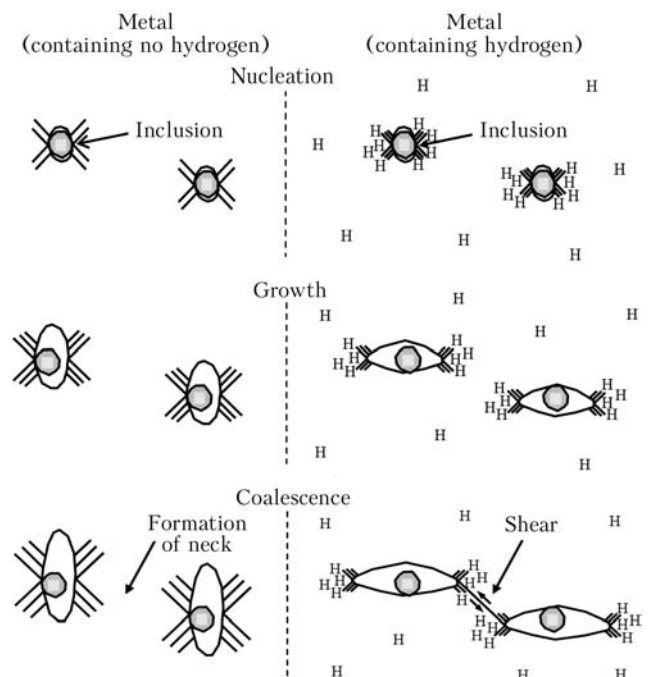


Figure 10. Scheme of nucleation, growth and merging of micropores in tough metal fracture

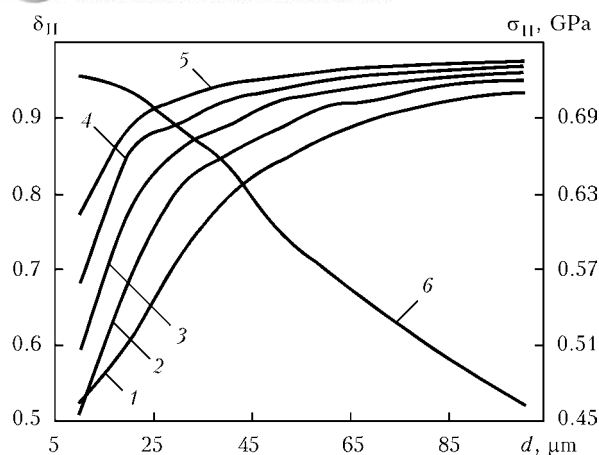


Figure 11. Dependence of degree of reduction of brittle strength of iron $\delta_H = \sigma_H / \sigma_0$ on grain size d at $T = 250$ (1), 275 (2); 300 (3), 325 (4) and 350 (5) K (σ_0 , σ_H – fracture stress of iron grain containing no hydrogen and containing, it respectively), and dependence σ_H of on d at $T = 300$ K (6)

Model of nucleation and growth of submicrocrack in metal grain on microcleavage mechanism was proposed considering the model of hydrogen transfer by dislocations. The main mechanism of metal embrittlement by hydrogen is effect of hydrogen-enhanced localized plasticity [47] which is considered through change of elastic energy of edge dislocations and submicrocrack induced by accumulation of hydrogen atoms around them. The effect indicated above significantly reduces value of stress necessary for grain fracture. Proposed mathematical model [57, 58] considers metal temperature, grain size in which submicrocracks appear, complex stressed state, physical characteristics of metal, mobility and concentration of diffusion hydrogen, speed of movement of edge dislocations and influence hydrogen-enhanced localized plasticity. Multi-factor model allows describing such peculiarities of reversible hydrogen embrittlement as tempera-

ture-speed dependence of value of fracture stress of metal containing hydrogen.

Computer modeling of influence of metal grain orientation in relation to external stresses on value of fracture stress was carried out [59]. The optimum angle of inclination between slip plane of edge dislocations and main tensile stress α_{opt} equals 45° . It is determined that number of dislocations in cluster reduces with deviation of inclination of slip plane of edge dislocations from optimum angle or increase of complex stressed state of metal. Appearance of cluster of edge dislocations in slip plane is completely impossible under certain conditions. Such a dependence between α_{opt} corresponds with conclusions of dislocation theory. It is determined that relative effect of hydrogen on metal brittle strength increases with rise of complex stressed state of metal, however, absolute value of fracture stress of hydrogen-containing metal grain increases.

Hydrogen-enhanced localized plasticity of metal significantly reduces value of stress which is necessary to be applied for grain fracture [57, 60]. In some cases decrease of metal strength can achieve 40–50 % (Figure 11). It was determined using calculations that, at other factors being equal, decrease of metal grain results in increase of degree of metal HE, however, absolute value of fracture stress of hydrogen-containing metal rises with grain decrease (see Figure 11, curve 6). Thus, increase of steel strength due to decrease of metal grain is reasonable only to certain extent, which depends on number of hydrogen as well as sensitivity of steel to HE under given conditions. Calculation results correspond with presented experimental data which were obtained for Armco-iron and low-carbon steel [12, 61].

One of the most possible mechanisms of macrocrack development in metal is formation microdefect in front of crack tip and its further coalescence with crack (Figure 12) [58, 62]. Area of plastic strains is formed in metal in front of tip of growing crack under effect of stress. In a process of crack growth this results in formation of plastically deformed metal under its surface, the thickness of which depends on applied stress, i.e. the higher stress which is necessary to be applied for formation of microdefect in front of crack tip, the thicker is the layer. Energy necessary for macrocrack growth consists from two parts, namely energy of formation of free surfaces, and energy of near-surface plastically deformed metal. In metal containing no hydrogen specific energy necessary for formation of such a layer is several orders higher than the specific energy of free surfaces of crack [63]. Stress nec-

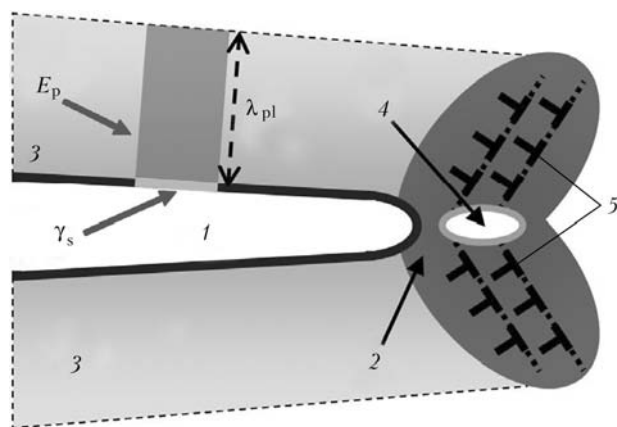


Figure 12. Scheme of growth of macrocrack in metal containing hydrogen: 1 – macrocrack; 2 – area of plastic deformations; 3 – subsurface layer of plastically deformed metal; 4 – microdefect; 5 – dislocation cluster; E_p – energy necessary for plastic strain of layer of metal of λ_{pl} thickness; γ_s – specific surface energy



essary for formation of microdefect in front of tip of macrocrack significantly reduces due to effect of hydrogen-enhanced localized plasticity. Effect of hydrogen-enhanced localized plasticity reduces the most energy-consuming constituent of macrocrack growth, i.e. formation of near-surface layer. Therefore, development of macrocrack should take place more brittle, with lower energy consumption in hydrogen-containing metal with BCC lattice that is observed in experiments [2, 12, 64].

Conclusions

1. Physical model of saturation of metals by gases being in contact with low-temperature plasma was developed. The model is build on the basis of kinetics theory of gases and considers movement of ions, atoms and molecules in plasma volume, adsorption and desorption of gas on metal surface as well as diffusion transfer of dissolved gas in metal melt.

2. It is shown that activation of molecules in plasma (excitation, dissociation, ionization) increases speed of dissolution by several orders in comparison with equilibrium conditions.

3. It is determined that entering of fluorine compounds in composition of welding consumables results in HF formation. Thermal-dynamic analysis showed that HF is substantially dissociated in larger part of arc section (high-temperature). Bonding of fluorine by hydrogen takes place in arc periphery that results in reduction of hydrogen absorbed by weld pool. Presence of HF in arc zone was experimentally proved.

4. New chromatographic methods for analysis of hydrogen in metal of welds, welding consumables and their components were proposed. Chromatographic method for analysis of diffusion hydrogen with degassing temperature up to 150 °C was entered in GOST 23338–91.

5. Method for reduction of hydrogen content in coated electrode welding and submerged arc welding providing extremely low concentrations of diffusion hydrogen in weld metal was proposed.

6. It is stated based on experiment-calculation investigations of kinetics of degassing of hydrogen from the weld metal that dependence of coefficient of diffusion on concentration of hydrogen is character for undeformed metal whereas it is not observed in deformed specimen. This is well settled in scope of ideas about dislocations as hydrogen traps.

7. It is determined that formation of hydrogen-induced cold cracks in welded joints is representation of HE under specific conditions of

thermal-deformation welding cycle. Therefore, solving of problem of HICC should be based on accurate knowledge of mechanism of HE of metal of the welded joint.

8. It is shown with high reliability that interaction of hydrogen with dislocations makes a basis of mechanism of HE. Hydrogen influences on nucleation and growth of microcracks in metal facilitating coalescence of dislocations that result in localized plastic strain under effect of hydrogen.

9. Effect of hydrogen on nucleation of microcrack in macrolevel appears in a form of reduction of normal tensile stresses necessary for its nucleation. Further growth of microcrack takes place on quasi-brittle mechanism due to formation of new microdefect in its tip under hydrogen effect.

10. It is shown with the help of computer calculations that quantity of hydrogen transferred by dislocations to the place of microdefect nucleation depends on speed of dislocation movement, metal temperature and has maximum in area of room temperatures. This is agreed with experimentally stated temperature-speed dependence of reversible HE having minimum in area of room temperature.

11. Modeling of growth of submicrocrack in metal grain considering effect of hydrogen-enhanced localized plasticity showed that metal becomes more brittle and sensitive to HE with reduction of size of grain, however, absolute value of fracture stress increases.

12. It is shown that removal of hydrogen from metal as well as its redistribution between diffusion and residual ones due to presence in metal of hydrogen traps take place in welded joint cooling. Increase of bond energy of traps and hydrogen reduces diffusion of the latter and increases quantity of residual hydrogen.

1. <http://www.worldsteel.org>
2. Pokhodnya, I.K., Yavdoschin, I.R., Paltsevich, A.P. et al. (2004) *Metallurgy of arc welding*. Kiev: Naukova Dumka.
3. Beloglazov, S.M. (1975) *Hydrogenation of steel in electrochemical processes (Review)*. Leningrad: LGU.
4. Kasatkin, O.G. (1994) Peculiarities of hydrogen embrittlement of high-strength steels in welding (Review). *Avtomatich. Svarka*, **1**, 3–7.
5. Yuhnovsky, P.I., Tkachev, V.I. (1987) About state of hydrogen in metal. *Fiz.-Khimich. Mekhanika Materialov*, **4**, 107–108.
6. Shvachko, V.I. (2002) *Reversible hydrogen brittleness of bcc iron alloys — structural steels*: Syn. of Thesis for Dr. of Phys.-Math. Sci. Degree. Kharkiv.
7. Teus, S.M., Shivanyuk, V.N., Shanina, V.D. et al. (2007) Effect of hydrogen on electronic structure of fcc iron in relation to hydrogen embrittlement of austenite steels. *Phys. Status Solids A*, **204**(12), 4249–4258.



8. Gavriljuk, V.G., Shivanyuk, V.N., Shanina, B.D. (2005) Change in the electron structure cause by C, N and H atoms in iron and its effect on their interaction with dislocations. *Acta Materialia*, **53**, 5017–5024.
9. Pokhodnya, I.K., Shvachko, V.I. (1997) Physical nature of hydrogen-induced cold cracks in welded joints of structural steels. *Avtomatch. Svarka*, **5**, 3–12.
10. Pokhodnya, I.K. (1998) Problems of welding of high-strength low alloy steels. In: *Current materials science of 21st century*; Transact. Kiev: Naukova Dumka, 31–69.
11. Geld, P.V., Ryabov, R.A. (1974) *Hydrogen in metals and alloys*. Moscow: Metallurgiya.
12. Kolachev, B.A. (1985) *Hydrogen brittleness of metals*. Moscow: Metallurgiya.
13. Yavdoshchin, I.R. (1969) *Investigation and development of universal electrodes with rutile coating*; Syn. of Thesis for Cand. of Techn. Sci. Degree. Kiev.
14. Pokhodnya, I.K., Shvachko, V.I., Portnov, O.M. (2000) Mathematical modelling of absorption of gases by metal during welding. *The Paton Welding J.*, **7**, 11–16.
15. Pokhodnya, I.K. (2003) Mathematical modelling of processes of interaction of metal with gases in arc welding. *Ibid.*, **2**, 2–9.
16. Pokhodnya, I.K., Portnov, O.M. (2003) Mathematical modelling of absorption of gases by electrode drop metal. *Ibid.*, **6**, 2–5.
17. Pokhodnya, I.K., Portnov, O.M., Shvachko, V.I. (2001) Computer modeling of hydrogen absorption by electrode metal drop under its intensive evaporation. In: *Proc. of 6th Seminar on Numeric Analysis of Weldability* (Graz, Oct. 2001). Graz: TU of Graz, 895–902.
18. Pokhodnya, I.K., Shvachko, V.I., Utkin, S.V. (1998) Calculated assessment of hydrogen behavior in arc discharge. *Avtomatch. Svarka*, **9**, 4–7.
19. Pokhodnya, I.K., Tsybulko, I.I., Orlov, L.N. (1993) Influence of slag composition on hydrogen content in liquid metal during CO₂ welding. *Ibid.*, **11**, 8–14.
20. Tsybulko, I.I. (1993) Calculation of thermodynamic equilibrium in metallurgical system gas-slag-metal. In: *Proc. of 2nd Int. Seminar on Numeric Analysis of Weldability* (Graz-Segau, 10–12 Sept. 1993). Graz: TU of Graz.
21. Pokhodnya, I.K., Shvachko, V.I., Ustinov, V.G. et al. (1972) Mass-spectrometric examinations of fluorides emitted in arc welding. *Avtomatch. Svarka*, **6**, 10–12.
22. Pokhodnya, I.K., Shvachko, V.I. (1981) Formation of hydrogen fluoride in arc discharge. *Ibid.*, **2**, 11–13.
23. Pokhodnya, I.K., Paltsevich, A.P., Yavdoshchin, I.R. (1986) Influence of methods of weld metal sampling for determination of diffusion-mobile hydrogen content in it. *Ibid.*, **1**, 24–28.
24. Pokhodnya, I.K., Paltsevich, A.P., Yavdoshchin, I.R. (1988) Influence of welding conditions on hydrogen content in welds made with electrodes of basic type coatings. *Ibid.*, **3**, 19–22.
25. Paltsevich, A.P. (1999) Chromatographic method of hydrogen content evaluation in electrode coating components. *Ibid.*, **6**, 46–48.
26. Pokhodnya, I.K., Paltsevich, A.P. (2003) Examination of potential content of hydrogen. In: *Abstr. for Int. Conf. on Current Problems of Welding and Resource of Structures* (Kiev, 24–27 Nov. 2003). Kiev: PWI, 67.
27. Panasyuk, V.V. (1991) *Mechanics of quasi-brittle fracture of materials*. Kiev: Naukova Dumka.
28. Paltsevich, A.P. (1988) *Development of methods of hydrogen content reduction in welds for new coated electrodes and flux-cored wires of basic type*; Syn. of Thesis for Cand. of Techn. Sci. Degree. Kiev.
29. Pokhodnya, I.K., Demchenko, L.I., Paltsevich, A.P. et al. (1976) Kinetics of diffusion redistribution of hydrogen between weld metal and base metal in arc welding. *Avtomatch. Svarka*, **8**, 1–5.
30. Pokhodnya, I.K., Demchenko, V.F., Demchenko, L.I. (1979) *Mathematical modeling of gas behavior in welds*. Kiev: Naukova Dumka.
31. Pokhodnya, I.K., Pavlyk, V.A., Shvachko, V.I. (1993) Effect of heat treatment and deformation on hydrogen diffusion and permeability of 10KhN3DM type steel. In: *Metallurgy of welding and consumables*. St.-Petersburg: StPGTU, 158–160.
32. (2011) *Development of materials for welding of technological equipment of mining and smelting and fuel and energy complexes*. Pt 1: Study by methods of experimental and numerical modeling of hydrogen behavior in weld metal of higher strength under conditions of thermal-deformation cycle of welding; Final report No. 0107U0022787. Kiev: PWI.
33. Sinyuk, V.S., Stepanyuk, S.N. (2009) Interaction of hydrogen with dislocation structure of structural steel welded joints. In: *Proc. of Sci. Conf. on Mechanics of Fracture Materials and Strength of Structures* (23–27 June, 2009, Lviv). Lviv: FMI, 999–1002.
34. Stepanyuk, S.M. (2001) *Reversible hydrogen embrittlement in welding of high strength low-alloy steels*; Syn. of Thesis for Cand. of Techn. Sci. Degree. Kyiv.
35. Shvachko, V.I., Ignatenko, A.V. (2007) Model of transportation of hydrogen with dislocations. *The Paton Welding J.*, **2**, 24–26.
36. Ignatenko, A.V. (2007) Mathematical model of transportation of hydrogen by edge dislocation. *Ibid.*, **9**, 23–27.
37. Pokhodnya, I.K., Shvachko, I.V., Kotrechko, S.A. et al. (1999) A new method for quantitative determination of sensitivity of steels to hydrogen embrittlement. *Int. J. Mater. Sci.*, **34**(4), 538–543.
38. Shvachko, V.I., Stepanyuk, S.M., Pokhodnya, I.K. (2000) The evaluation methods of HSLA steels susceptibility to hydrogen embrittlement. In: *Proc. of 4th Int. Conf. on HSLA Steels* (Xi'an, China, Oct. 30–Nov. 2, 2000). Beijing: Metallurg. Industry Press, 453–458.
39. Pokhodnya, I.K., Meshkov, Yu.Ya., Shvachko, V.I. et al. *Method of quantitative determination of level of hydrogen embrittlement of structural steels and welds*. Appl. 5040067. Int. Cl. G 01 n 17/00. Fil. 01.07.91.
40. Meshkov, Yu.Ya. (1981) *Physical principles of strength of steel structures*. Kiev: Naukova Dumka.
41. Meshkov, Yu.Ya., Pakharenyko, G.A. (1985) *Structure of metal and brittleness of steel products*. Kiev: Naukova Dumka.
42. Meshkov, Yu.Ya., Serditova, T.N. (1989) *Fracture of wrought steel*. Kiev: Naukova Dumka.
43. Kotrechko, S.A., Meshkov, Yu.Ya., Mettus, G.S. (1990) To problem of tough and brittle states of polycrystalline metals. *Metallofizika*, **12**(6), 3–13.
44. Sinyuk, V.S., Pokhodnya, I.K., Paltsevich, A.P. et al. (2012) Experimental study of the mechanism of hydrogen embrittlement of metals with the bcc lattice. *The Paton Welding J.*, **5**, 8–11.
45. Tsaryuk, A.K., Brednev, V.I. (1996) Problem of cold crack prevention. *Avtomatch. Svarka*, **1**, 36–40.
46. Vladimirov, V.I. (1984) *Physical nature of metal fracture*. Moscow: Metallurgiya.
47. Birnbaum, H.K., Sofronis, P. (1994) Hydrogen-enhanced localized plasticity – a mechanism for hydrogen-related fracture. *Mat. Sci. and Eng. A*, **174**, 191–202.
48. Kotrechko, S.A., Meshkov, Yu.Ya. (2008) *Ultimate strength*. Kiev: Naukova Dumka.
49. Pokhodnya, I.K., Shvachko, V.I., Utkin, S.V. (2002) Effect of hydrogen on equilibrium of dislocation submicrocrack in α -iron. *Fiz.-Chimich. Mekhanika Materialiv*, **1**, 7–14.
50. Beachem, C.D. (1972) A new model for hydrogen-assisted cracking (hydrogen embrittlement). *Metallurg. Transact.*, **3**, 259–273.
51. Gedeon, S.A., Eagar, T.W. (1990) Assessing hydrogen-assisted cracking fracture modes in high-strength steel weldments. *Welding J.*, **6**, 213–219.



52. Sofronis, P., Liang, Y., Aravas, N. (2001) Hydrogen induced shear localization of the plastic flow in metals and alloys. *Eur. J. Mech. – A: Solids*, **20**, 857–872.
53. Liang, Y., Sofronis, P., Aravas, N. (2003) On the effect of hydrogen on plastic instabilities in metals. *Acta Materialia*, **51**, 2717–2730.
54. <http://www.icf.11.com/proceeding/EXTENDED/5638.pdf>
55. Liang, Y., Sofronis, P., Dodds, R.H. (2004) Interaction of hydrogen with crack-tip plasticity: Effect of constraint on void growth. *Mat. Sci. and Eng. A*, **366**, 397–411.
56. Ahn, D.C., Sofronis, P., Dodds, R.H. (2007) On hydrogen-induced plastic flow localization during void growth and coalescence. *Int. J. Hydrogen Energy*, **32**, 3734–3742.
57. Ignatenko, O.V., Pokhodnya, I.K. (2011) Influence of hydrogen-enhanced localized plasticity and grain size on the strength of bcc metal. In: *Proc. of 2nd Ukrain.-Greek Symp. on Fracture Mechanics of Materials* (3–7 Oct. 2011, Lviv). Lviv: FMI.
58. Ignatenko, A.V., Pokhodnya, I.K., Paltsevich, A.P. et al. (2012) Dislocation model of hydrogen-enhanced localizing of plasticity in metals with bcc lattice. *The Paton Welding J.*, **3**, 15–19.
59. <http://dfmn2011.imetran.ru/2011/index.php>
60. Ignatenko, O.V., Pokhodnya, I.K., Stepanyuk, S.M. et al. (2010) Principles of hydrogen cracking of welded joints of high strength low alloy steels. In: *Fundamental problems of hydrogen energy*. Kyiv: KIM, 340–360.
61. Ostash, O.P., Vitvitsky, V.I. (2011) Duality of hydrogen effect on mechanical behavior of steels and structural optimization of their hydrogen resistance. *Fiz.-Chimich. Mekhanika Materialov*, **4**, 4–19.
62. Ignatenko, A.V., Sinyuk, V.S. (2012) Influence of hydrogen-enhanced localized plasticity and complex-stressed state on strength of metal. In: *Proc. of 6th Int. Conf. on Mathematical Modelling and Information Technologies in Welding and Related Processes* (Katsiveli, 29 May–1 June 2012). Kiev: PWI, 35–36.
63. Panasyuk, V.V. (1968) *Ultimate equilibrium of brittle bodies with cracks*. Kiev: Naukova Dumka.
64. Morozov, L.S., Chechulin, B.B. (1967) *Hydrogen brittleness of metals*. Moscow: Metallurgiya.

Received 27.03.2013