THE ROLE OF THE INTERFACE REACTION IN THE KINETICS OF THE NONSTEADY-STATE PERMEATION OF HYDROGEN

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The role of the stage of hydrogen transition from the solid-phase surface to the bulk in the kinetics of the total process of hydrogen charging of a metal is considered for the general case of rate control. The quantitative description of the nonsteady-state hydrogen permeation based on the solution of a diffusion problem with boundary conditions of the third kind is suggested. Approximate formulas are proposed for the analysis of the data of electrochemical measurements of nonsteady-state hydrogen permeation in the diffusion problem aimed at calculation of the kinetic parameters of hydrogen absorption, desorption, and stages of diffusion. The results of theoretical analysis are checked by using the dependences of hydrogen permeation vs time recorded in the process of hydrogen charging of iron membranes in carbonate-bicarbonate solutions (pure and with inhibitors).

Introduction

The stage of transition of hydrogen from the adsorbed state into the absorbed state (hydrogen ingress, interface reaction) in the total process of hydrogen charging was analyzed for the first time in [1]. The effect of this transition on steady-state hydrogen permeation was quantitatively described in [2]. It is worth noting that the process of nonsteady-state hydrogen permeation was analyzed in [2] by using the Barrer equation. This means that, when analyzing the steady-state permeation current, the kinetics of the interface reaction was taken into account, whereas the nonsteady-state permeation current was considered within the simplest model neglecting the influence of hydrogen, i.e., the interface reaction. This contradiction was noticed and discussed in [3].

The contribution of the stage of hydrogen ingress into the kinetics of the process of hydrogen permeation was also noticed in the discussion of the experimentally observed apparent effect of the thickness of a membrane on hydrogen diffusivity in steel [4]. In [4], boundary conditions of the third kind were used in their simplest form excluding the reversibility of the hydrogen ingress stage. A similar approach was also presented in [5] and [6] in studying the process of hydrogen permeation through electrolytic nickel.

The kinetic constants of hydrogen ingress were estimated by using the data on steady-state hydrogen permeation accumulated during cathodic polarization of iron [7] and corrosion of C–Mn steel in Cl-containing solutions [8]. The effect of the phase-boundary reaction on the kinetics of nonsteady-state hydrogen permeation was studied in [9] and [10]. In these works, the changes in the shape of permeation curves caused by a finite rate of the hydrogen ingress stage were predicted by numerical calculations and compared with the experimental data. However, since we do not know any efficient method for the determination of the kinetic parameters of interface reactions, the application of the results obtained in [9] and [10] was seriously restricted and they could be used only for the purposes of qualitative explanation of experimentally observed relationships. The analysis of the parameters of hydrogen transition is especially important in the investigation of the effect of modification either of an aggressive solution or of the metal surface on the process of hydrogen charging of the metal.

In [11] and [12], two limiting cases were discussed for the process of hydrogen release from nonstationary charged iron, namely, transport (diffusion + trapping) control and interface control. By processing the current transient curves on the basis of proposed explicit expressions, the constants of equilibrium between the absorbed and dissolved hydrogen were estimated for different potentials, additions of H₂S to electrolytes, and various types of heat treatment of the electrodes.
In the present work, the role of hydrogen ingress in the kinetics of nonsteady-state hydrogen permeation is considered for a general case of rate control lying between the limiting cases of diffusion and interface controls. Approximate solutions of the diffusion problem are proposed to process the data on nonsteady-state hydrogen permeation obtained by electrochemical measurements to calculate the kinetic parameters of hydrogen ingress (adsorption–absorption transition) and hydrogen transport through the metal. The results of theoretical investigations were checked by experimental measurements of the effect of cathodic and anodic polarization and additions of inhibitors on the process of hydrogen uptake from carbonate–bicarbonate solutions.

Theoretical Investigations

In the classical method of electrochemical measurements of hydrogen permeation [2], the diffusion problem was solved with boundary conditions of the first kind. These conditions correspond to instantaneous changes in the surface concentration of hydrogen on the application of an external source of hydrogen. They can be experimentally satisfied by a proper polarization of the studied electrodes. However, this approach implies that the concentration of hydrogen on the metal surface in contact with electrolytes is similar to the concentration of hydrogen in the metal layer infinitely close to the phase boundary. This automatically excludes any consideration of the hydrogen ingress stage because the rate of hydrogen transition from the adsorbed into the absorbed state is assumed to be infinitely high. This restriction can be removed as indicated in what follows.

In Fig. 1, we present a schematic diagram of the considered problem of hydrogen transition across the interface and hydrogen diffusion through a metal membrane described by the following formula:

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\begin{array}{c}
H_{ad} \xrightleftharpoons{\frac{k_{ab}}{k_{d}}} H_{me}\{1\} \xrightarrow{k_{ad}} H_{me}\{0\},
\end{array}
\]  (1)