INVESTIGATION OF HYDROGEN PERMEABILITY OF ALUMINUM AND ITS PROTECTING PROPERTIES

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Introduction

Aluminum and its alloys are extremely important structural material in modern technology due to lightness combined with good mechanical properties, machinabillty and low cost. In hydrogen power engineering aluminum also could be employed because of the inert and strong aluminum oxide film on the surface. However Al_2O_3 film appearing at oxygen pressure $1.33 \cdot 10^{-5}$Pa [1], in combination with low hydrogen solubility [2-5], pose serious problems for investigation of hydrogen – aluminum interaction.

In present work the concentration pulse method was employed [6]. This method allows to determine a set of parameters of hydrogen-metal interaction taking into account bulk (diffusion and trapping) and surface processes. Investigation were carried out at temperatures 573-698K. Glow discharge in hydrogen atmosphere was used to achieve measurable hydrogen concentration in aluminum.

Experiment

A sample was aluminum membrane (99.5 wt.%) 0.5mm thick and 35mm in diameter. Construction of sample holder allowed heating up to 723K during prolonged time.

The electrodes disposed bilaterally along the membrane allowed to initiate a glow discharge in hydrogen and consequently irradiating both sides of membrane with hydrogen ions. Employing of thermal dissociator in the form of tungsten wire provided if necessary flux of atomic hydrogen on one of two sides of membrane.

Idea of the concentration pulse method is the following. At upstream side of membrane a series of rectangle pulses is generated (on-off time ratio equals 2, meanders). Such conditions can be realized by means of atomizer or glow discharge switching on and off at upstream side of membrane. Criterion of right model choice is the coincidence of experimental time dependence of permeating flux with theoretical one.

Results

The experiments with molecular hydrogen have shown that up to 673K and the hydrogen inlet pressure up to 6650 Pa there is no evidence of measurable permeating flux through the sample.

The use of hot tungsten filament as an atomiser has allowed for maintaining the flux of hydrogen atoms toward the sample surface at the order of $10^{19}H^0/m^2s$. Nevertheless, the exposition of upstream side with the hydrogen atoms at 673K did not lead to the appearance of measurable permeating flux.

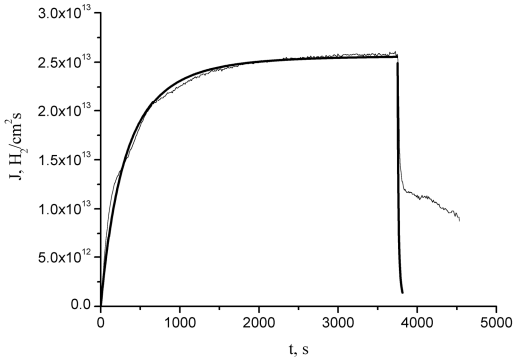

Fig.1 The typical kinetic curve of establishing of the steady state flux at on ignition and extinction of glow discharge (T=648K). Thin noisy line – experimental data, bold smooth line – theoretical curve.

On ignition of glow discharge on the upstream side of membrane the significant permeation flux has been found. The typical kinetic curve of establishing of the steady state flux at 648K is sketched on fig.4 (the thin nosy line). After the steady state flux has been achieved, the discharge was switched off and the decay of permeating flux has been observed. The clear asymmetry of advanced and rear fronts (i.e. the kinetics of flux growth on ignition and the decay on extinction of discharge) draws an essential attention in displayed curve.

When aluminum has been investigated by concentration pulse method, we had to use the following trick. At the onset on the upstream side of membrane the glow discharge with current density I_0=5.9mA/cm^2 has been ignited in the hydrogen medium. After the steady state flux has been achieved, the oscillations of current have

been arranged in accordance to the following law $I(t)=I_0+\Delta I(t)$, where $\Delta I(t)$ is periodical additional current changed by the law of square-wave pulses.

As the result the time dependence of permeating flux has the form of periodically changing small amendment on the significant steady state flux (fig.2). Due to periodicity of established process there is a possibility of averaging the curves over several periods.

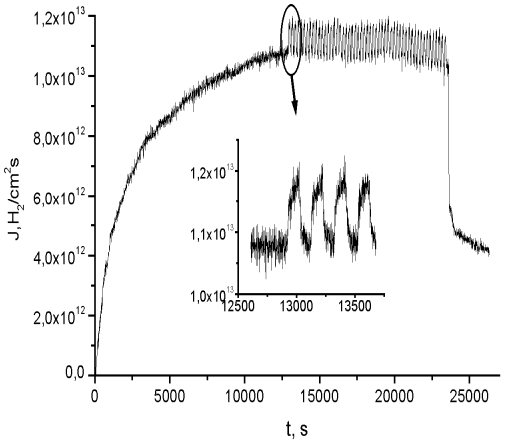

fig.2. Kinetic of permeation flux have been measured in concentration pulse method (T=598K).

Discussion

To describe the kinetic curves of establishing of the steady state flux the model of impeded desorption both on upstream and downstream side of membrane (model of potential box) have been adopted:

$$\frac{\partial C}{\partial t} l = J_{ab} - b_1^* C^2 - b_2^* C^2, \; J_{perm} = b_2^* C^2$$

Where t – time, x – spatial co-ordinate, C – concentration of hydrogen, $b_{1,2}^*$ - rate constants of desorption from up- and downstream membrane sides respectively, J_{ab} – absorption hydrogen flux at upstream side , J_{perm} – permeating hydrogen flux, l – thickness of membrane .

Simulations on this model show that it allows to trace the differences between the advanced and rear fronts as well as for the fair description of advanced front. Mean value of desorption rate constant found in the approximation is of $b^*=8\cdot10^{-28}m^4/s$.

Treating experimental results obtained by concentration pulse method, various models had been considered in the simulations. The model of potential box supplied with the reversible trapping of hydrogen in the membrane bulk yields a satisfactory coincidence of theory and experiment. However, for the best fitting of experimental curves it was necessary to take into account the finiteness of hydrogen diffusion rate in aluminum.

The data processing for the model has allowed for measuring the temperature dependence of diffusion coefficient of hydrogen in aluminium: $D=(4\pm2)\cdot10^{-4}[m^2/s]\cdot exp(-(50\pm4)[kJ/mole]/RT)$. It was not possible to determine the activation energies of other processes since the investigated temperature interval was just 125K. In the temperatures (573-698K), the desorption rate constant was about $b^*\approx1,5\cdot10^{-28}m^4/s$, the trapping rate constant was $r\approx0,1s^{-1}$, and the detrapping rate constant was $b\approx0.2s^{-1}$.

Protecting properties of aluminum coating deposited on stainless steel membrane were investigated. It was found that hydrogen permeability of 0.2mm thick membrane made from 12X18H10T steel decreases more than for two orders of magnitude due to aluminum coating.

Conclusion

We have investigated the parameters of hydrogen permeating through aluminum by means of concentration pulse method. For formation of concentration pulses, the method of glow discharge current changing has been implemented on the upstream side of membrane. The model of hydrogen transport in aluminum includes diffusion coming along with reversible trapping and the associative desorption on the upstream and downstream sides. The figures of parameters of model have been found:

Diffusion coefficient

$D=(4\pm2)\cdot10^{-4}[m^2/s]\cdot\cdot exp(-(50\pm4)[kJ/mole]/RT)$.

In the temperatures (573-698K), the desorption rate constant: $b^*\approx1,5\cdot10^{-20}cm^4/s$.

The trapping rate constant: $r\approx0,1s^{-1}$.

Detrapping rate constant was $b\approx0.2s^{-1}$.

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