Investigation of hydrogen permeability through nickel membrane by mass spectrometry method

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Abstract. Dynamics of hydrogen permeability through nickel membrane is studied; diffusion coefficient and time of hydrogen penetration through membrane are calculated. As a result of the work, it was revealed that hydrogen diffusion through the nickel membrane occurs, and it has a saturation character one day after the application of the solution. The obtained results make it possible to evaluate the process of flooding of quartz resonators of thermostats (QRT) housings in a chemically aggressive environment and in conditions of high humidity.

1. Introduction
Increasing the degree of integration of modern microcircuits imposes increased requirements on the quality of the surface of crystals and internal surfaces of housings to limit negative surface processes leading to degradation of electrical parameters, and corrosion of metal contacts and conductors [1]. As is known, the presence of hydrogen in metals changes their electrical, magnetic, mechanical and corrosive properties. Therefore, the development of scientifically sound measures to combat such problems requires accurate information on the solubility and diffusion rate of hydrogen in the materials under study. The study of the interaction of hydrogen with the metal surface is one of the most important directions in this area. At the same time, the data of different authors differ significantly, especially at low and room temperatures, where direct measurements are difficult to make. When examining the hydrogen content of various materials, it is generally believed that the penetration of hydrogen into the metal is limited by the presence of an oxide on the surface of the test sample. However, this assumption cannot be considered fully proven, since when studying the process of hydrogen diffusion in metals, it is difficult to separate surface and volume effects; this does not allow the nozzles to provide the data available in the literature for different transition metal surface oxides.

Despite a huge number of works devoted to the study of the development of metal-hydrogen systems, the methodology for the study of hydrogen diffusion processes in surface oxide layers is not well developed. The numerical values of the hydrogen diffusion coefficients obtained by different authors even for one metal differ by several orders of magnitude, and for the corresponding oxides - by more than 10 orders of magnitude. Such significant differences are obviously due to the presence of a number of complex controlled factors (formation of surface hydrides, dependence of the diffusion coefficient on the concentration of hydrogen in the metal, etc.), which are not taken into account when
numerical processing of the results and determining the diffusion coefficient of hydrogen in the metal [2].

To study the diffusion of hydrogen or hydrogen permeability of metals, a metal plate is used - a membrane that separates two vessels representing the inlet side and the registration side. The penetration of hydrogen through the metal membrane is a chain of followers of processes occurring both on the surface of the metal and in its volume. It includes adsorption, absorption, diffusion and desorption processes [3]. Once a certain distribution of hydrogen in the membrane has been established, the change in the concentration or rate of hydrogen influx on the input side occurs with some time lag in the measured signal on the registration side. The time lag depends both on the mobility of the diffusing particles in the metal and on the rate of transfer across the phase boundaries. In this regard, it is also possible to classify methods for studying flooding depending on the pressure of hydrogen on the inlet and registration sides. At high temperature, when large flows of hydrogen can be created, gas volumetric methods are usually used [5]. But as noted in the work, due to low accuracy, the method finds only limited use.

To increase accuracy, pressure is measured in pre-pumped cavity with the help of manometric lamps, or ion current measurements of mass spectrometer [6] are used. Thus, a vacuum/atmosphere system separated by a metal membrane can be used to determine the diffusion coefficient of hydrogen. Modern chips are usually closed in special enclosures, for example, metal (nickel), which are in a protected atmosphere, or evacuated for stable operation over the entire service life. For quartz resonators of thermostats, casings of type DIP-14 or DIL -14 [7] are used. For stable and long-term operation (more than 20 years), the housings are subject to high requirements, both for cleanliness of internal surfaces and tightness, including hydrogen permeability [8, 9].

The purpose of this work is to study the dynamics of hydrogen permeability through the nickel membrane by mass spectrometry.

2. Experimental setup

The vacuum system consisted of a high-vacuum pump NMDO-0.25-1 (NORD 250), a magnetron sensor consisting of a vacuum meter VMB-8, a vacuum pump 2NVR-5DM, a residual gas analyzer (RGA) XT-100, connecting flanges and valves.

The nickel membrane (in the form of a cuvette) was pressed against a copper gasket, which was clamped by steel washers on the connecting flange. After pre-pumping with a vacuum pump, a long-term pumping with a magnetic discharge vacuum pump NORD-250 followed. Subsequently, when the pressure in the vacuum chamber reached values of the order of $5 \times 10^{-6} - 5 \times 10^{-7}$ torr, the spectra of residual gases were removed, followed by their decoding.

Results and discussions

A 5% sulfuric acid solution with an acidity of $P_H = 0.05$ was selected as the hydrogen source. Using a pipette, 1 ml of solution was placed on the membrane. During the experiment, a constant amount of solution in the cuvette was maintained. The temperature was also controlled, which was $T = 22 ^\circ C$. Measurements were performed regularly for 7 days. Figure 1 shows the mass spectra of the residual gases after the membrane installation (figure 1(1), $P=1 \times 10^{-6}$ torr), and after prolonged pumping (figure 1(2), $P=7 \times 10^{-7}$ torr) until acid solution is added. It can be seen that after a long pumping, a decrease in peaks of $18$ a.m.u. ($H_2O$), $28$ a.m.u. ($N_2^+$) and $32$ a.m.u. ($O_2^+$), at the same time additional peaks do not appear due to the presence of nickel membrane and contaminant on it.
Figure 1. Mass spectrum of residual gases. 1 – on the first day, 2 – spectrum after long pumping.

A feature of the device software is the tracking of the masses of interest in the form of trend lines over a certain period of time. Figures 2 and 3 show trend lines H and H₂ with recording time 10 and 20 minutes, respectively. Since the dynamics of hydrogen penetration through the membrane was interested, this type of representation is justified. The graph shows that the hydrogen concentration is slightly reduced, given the continuous pumping by the magnetic discharge pump, it is possible to conclude that there is a constant influx of hydrogen, possibly only through the membrane.

Figure 2. Hydrogen trend line in 10 minutes. Figure 3. Hydrogen trend line in 20 minutes.

Since the partial pressure of hydrogen varies slightly due to the relatively low temperature of the membrane, it has been proposed to measure it every hour during the working day. The dynamics of the relative pressure of molecular hydrogen by hour on different days is shown in figure 4. Figure 4 (8.10) shows the hydrogen pressure dynamics before the solution is applied to the membrane. The graph clearly shows a strong increase in hydrogen content in the vacuum system, after the start of the experiment, figure 4 (12.10). Every day, in the following hours, there is a decrease in hydrogen content (13.10, 14.10), which is possibly due to the formation of nickel sulfate (NiSO₄) on the surface of the membrane, which is extremely hygroscopic. Therefore, a change in solution concentration and membrane properties can be mentioned. To maintain the experimental conditions, the membrane surface was cleaned and a fresh sulfuric acid solution was added (see figure 4 (15.10-16.10)), but a decrease in the level of relative hydrogen concentration in the system continued.
The dynamics of the relative part of H in the system during the week is shown in figure 5. It can be seen that the proportion of hydrogen during observation increased by about 65%, from which it can be made that its source in the system can be the penetration of H⁺ from a solution of sulfuric acid.
Figure 6 shows the change in hydrogen partial pressure by day. The penetration process can be conditionally divided into two stages. At the first stage, due to hydrogen adsorption at the inlet side, rapid diffusion and low desorption rate at the outlet side, the dissolved hydrogen concentration increases uniformly throughout the thickness of the sample (2-4 day). There is also an increase in hydrogen desorption flow from the outlet side of the membrane, since it is associated with the concentration of dissolved hydrogen [10]. At the second stage, with further accumulation of hydrogen in the membrane, the concentration in the solution reaches the level of maximum solubility. At that formation of nucleation of hydride phase in membrane volume begins, and concentration growth in solution stops. We estimate the diffusion coefficient of hydrogen through the membrane. Dependence of diffusion coefficient in nickel on temperature is described by formula [11]:

$$D_{Ni} = 6.7 \cdot 10^{-3} \exp \left( -\frac{9.5 \text{ kcal/mole}}{RT} \right) \frac{cm^2}{s}.$$  

Then, at temperature $T = 295$ K, the diffusion coefficient of hydrogen is:

$$D_{Ni}(295 \text{ K}) = 6.43 \cdot 10^{-10} \frac{cm^2}{s}.$$  

The permeation time of hydrogen through the membrane can be estimated [12]:

$$\tau = \frac{d^2}{\pi^2 \cdot D_{Ni}} \cdot \ln \left( \frac{2}{1 - \alpha} \right) \approx 0.87 \cdot 10^5 \text{ s},$$

where $d$ is the thickness of the membrane ($d = 0.02 \text{ cm}$), $\alpha$ is the fraction of stationary flow after a hopping change in hydrogen concentration ($\alpha > 0.2$). As a result, the time of hydrogen penetration through the membrane is slightly more than 24 hours at a temperature of $T = 22 \degree \text{C}$, which is indirectly confirmed experimentally (figure 6) - exit at the saturation level occurs on the second day after the solution is applied to the membrane. Thus, after the membrane is initially saturated with hydrogen ions, the dynamics of its drift from the outer boundary of the membrane to the internal contact with the vacuum can be traced.
Conclusion

In the course of the work, the following tasks were performed: assembly and installation of a vacuum system for mass spectrometry studies, study of the spectrum of residual gases of the vacuum system, study of the dynamics of hydrogen permeability through the nickel membrane, calculation of the diffusion coefficient and the time of hydrogen penetration through the membrane. As a result of the work, it was revealed that hydrogen diffusion through the nickel membrane occurs, and has a saturation character a day after the application of the solution. The obtained results make it possible to evaluate the process of flooding of QRT housings in chemical aggressive ambient and in conditions of high humidity.

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