Features of hydrogen diffusion through an amorphous Fe$_{92}$Si$_6$B$_2$ alloy membrane

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Abstract. In this work, the hydrogen diffusion through an amorphous Fe$_{92}$Si$_6$B$_2$ alloy membrane has been investigated. It has been established that the hydrogen diffusion decreases with the growth of the acidity of the environment at the constant ionic force of solution. The probable mechanisms of the blocking of hydrogen flow through the membrane have been discussed. An insignificant variation of the mechanical characteristics (ultimate tensile strength, microhardness, Young’s modulus) of Fe$_{92}$Si$_6$B$_2$ amorphous alloy has been detected.

1. Introduction

Amorphous magnetically soft metallic alloys with the low coercive force and the high magnetization are intensively used as the transformer cores, the generators in the different sensors [1-4] etc. While using, they are impacted to different factors such as the action of corrosion and hydrogen-containing mediums. It is known that corrosion and hydrogenation are practically impossible for elimination [5-7]. The corrosion destructions, coursing with the hydrogen depolarization (by the impact of the acidic solutions), are the most common in practice [8-11].

Amorphous metallic alloys have a noticeable sensitivity to the embrittling influence of hydrogen [12, 13]. A criterion of hydrogenation for metallic alloys is caused by the diffusion capacity of hydrogen. That can be determined by a measuring of the current density of diffusing hydrogen through the membrane that was made from investigated alloy.

The goal of the work is in a study of hydrogen diffusion through the membrane, made from amorphous Fe$_{92}$Si$_6$B$_2$ alloy, as well as in the measuring of changing of the mechanical characteristics of that membrane (ultimate tensile strength, plasticity, microhardness, Young’s modulus) after the impact of hydrogen-containing mediums.

2. Materials and methods

While the experiments, we used Fe$_{92}$Si$_6$B$_2$ amorphous metallic alloy. The hydrogen diffusion through the membrane with area 3.63·10$^{-4}$ m$^2$ and thickness 25 μm was studied in the Devanathan two-compartment cell. The integral value of the hydrogen current through the membrane was determined by the method [12]. We used HCl solutions with concentration 0.1; 0.5; 0.99 mol/l. For the maintaining constancy of the ionic force, we injected LiCl additionally in the solutions. We determined change of the mechanical properties of the specimens on the Instron-5565 electromechanical machine for the static experiments. We investigated surface elemental composition...
by the x-ray photoelectron spectroscopy (XPS) method with the SPECS UNI-SPECS photoelectron spectrometer. We investigated surface morphology of the specimens on the Merlin electron microscope. We measured microhardness by the PMT-3M tester. We determined a plasticity factor of alloy by the bending method [14].

3. Discussion of results
We investigated a relation of the current density of diffusing hydrogen through the membrane without the cathode polarization from the concentration of work solution (figure 1).

![Figure 1. A relation of the integral hydrogen current density from the hydrogen concentration in the work solution.](image1)

It has been determined that the average current density of diffusing hydrogen decreases through the membrane from amorphous alloy at the increase of the environment acidity with the constant ionic force of solution. For an explanation of the probable mechanism of the hydrogen current blocking through the amorphous membrane, FeCl₂ compound (a Cl-spectral line with its compounds occurs only for the 2nd specimen – see figure 2) that may shift to Fe₃O₄ compound by the chain of reactions: Fe + 2HCl = FeCl₂ + H₂↑, with the next hydrogen partial hydrolysis of ferrous chloride (II): FeCl₂ + HOH = Fe(OH)Cl + HCl, and interaction of the forming iron compounds one another and with molecular oxygen, dissolved in work solution: FeCl₂+4Fe(OH)Cl+O₂ = Fe₂O₃ + 2FeCl₃ + 2H₂O, is held as the most important. The pointed reactions also can be presented by the ionic equations: Fe + 2H⁺ = Fe²⁺ + 2Hads; Hads + Hads = H₂↑; 4Fe²⁺+6H₂O+O₂ = 4FeO(OH) + 8H⁺; Fe²⁺+4Fe(OH)⁺ +O₂ = Fe₃O₄ + 2Fe³⁺ + 2H₂O; Fe³⁺ + HOH = Fe(OH)⁺ + H⁺, where Hads – adsorbed hydrogen. It is necessary
to point out that FeCl$_2$ compound occurs only on the XPS spectra for the 2$^{nd}$ specimen (the spectral line 199 eV) [15]. Consequently, the formation of Fe$_3$O$_4$ oxide and FeO(OH) oxyhydroxide occurs on the surface of material during the impact of hydrogen-containing medium (figures 2,3) [16, 17]. Fe$_3$O$_4$ and FeO(OH) compounds can block access of hydrogen to metal, forming the surface dense layer. Herewith, the oxidation process can continue until completely dissolve of the specimen. For the most studied concentration of hydrochloric acid, discharge reaction comes with the maximum rate, and then produced atomic hydrogen forms H$_2$ molecules and comes to the gaseous phase. For this case, the whole process is limited, probably, by the stage of nucleation of a gas bubble on the metallic surface. Herewith, surface active centres are blocked by the products of iron interaction with work solution, for this reason, the solid-state diffusion process occurs with a low rate in comparison with the molecular hydrogen forming. While the decrease of the concentration of HCl, the rates of the solid-state diffusion and forming of molecular hydrogen are comparable because not all adsorbing centres are blocked by the corrosion products of iron. For this case, the hydrogen diffusion flow will more than in case of the maximal concentration, as a result of equalization in rates of the coursing parallel processes. Note, that the pointed equations of the chemical reactions describe the hypothetic reaction paths of the forming of iron (III) compounds, but comprehensive study of the process will possible after the electrochemical and impedance measurements.

![Figure 4](image-url)  
**Figure 4.** A view of the fracture for Fe$_92$Si$_6$B$_2$ amorphous alloy after the deformation: a) hydrogen concentration 0 mol/l; b) hydrogen concentration 0.5 mol/l HC1+0.5M LiCl; c) branching in the apex of the crack of Fe$_92$Si$_6$B$_2$ amorphous alloy after the mechanical deformation (hydrogen concentration 0.5 mol/l HC1+0.5M LiCl); d) forming of the creases on the surface (hydrogen concentration 0.99 mol/l HC1+0.01M LiCl).

It has been established experimentally, that the mechanical properties of iron-based amorphous alloy change after the treatment of hydrogen-containing medium. The morphological features of the destruction process of iron-based amorphous alloy at the uniaxial tension test have been investigated (figure 4 a, b) after the experiments on hydrogen diffusion. While the fracture, the branching cracks (figure 4 c) and creases (figure 4 d) are forming. While the branching of crack on the surface of the specimen, the ledges, whose sizes range from 200 to 700 nm, forming. On the destruction surface, the typical «venous» pattern is observed [18].
While the increase of the hydrogen concentration, the deformation relief does not change significantly and the deformation also comes with the forming of the creases whose size range up to ~1 μm. While the contact of alloy with hydrogen medium, the film from potassium and manganese oxides with the «scaly» structure (figure 5 a) forms on the surface of specimens, from the side that is opposed to the surface with the HCl impact. The processes of the stratification in specimen take place (figure 5 b).

![Figure 5 a](image1)
![Figure 5 b](image2)

**Figure 5.** Fe$_{92}$Si$_6$B$_2$ amorphous alloy: a) the potassium and manganese oxides, that formed on the surface of alloy; b) the formation of the layer structures. Work solution 0.99 mol/l HCl + 0.01M LiCl.

It has been established experimentally, that the impact of hydrogen mediums of the pointed concentrations changes the tensile strength of iron-based amorphous alloy. While the low hydrogen concentration (0.1 mol/l HCl + 0.9 M LiCl), the tensile strength slightly decreases on ~ 5%. While the further increase of hydrogen concentration, the tensile strength increases by around 20% (figure 6).

![Figure 6](image3)

**Figure 6.** Changing of the tensile strength ($\sigma$) and microhardness ($H_v$) in membranes from Fe$_{92}$Si$_6$B$_2$ amorphous alloy, induced by hydrogen diffusion. Every point has been plotted after 10 measurements.

Young’s modulus changes in a range of the measurement error and it is ~86 GPa. Microhardness of the investigated specimens decreases in a range of 10% at the increase of HCl concentration and decrease of LiCl concentration.

A study of the specimens by the bending method has shown that the $\varepsilon$ plasticity parameter, that is determined by the formula: $\varepsilon = h/(D - h)$, wherein $h$ – is the thickness of ribbon-like specimen, $D$ – is the distance between the parallel plates, is the constant in the range of the measurement error and it equals to 1 because the specimens do not destruct during the bending tests. It testifies that the embrittlement of alloy does not occur practically by the hydrogen impact during pointed time intervals. Hydrogen, diffusing through a membrane from amorphous metallic alloy, leads to the forming of oxides but it does not generate the embrittlement.
4. Conclusion
It has been established that hydrogen diffusion current through the membrane from Fe$_{92}$Si$_6$B$_2$ amorphous alloy depends on acidity of medium, and it (current) decreases while acidity increases at the constant ionic force. While the increase of HCl concentration in work solution, Fe$_3$O$_4$ and FeO(OH) compounds, blocking the hydrogen diffusion current, are forming on the surface of alloy. Formed atomic hydrogen recombines and comes to the gaseous phase. While the decrease of HCl concentration, rate of the forming of oxide and oxyhydroxide decreases and the hydrogen diffusion current increases. The insignificant changing of the mechanical parameters of alloy permits to make a conclusion that hydrogen does not make the embrittlement impact on amorphous alloy at the pointed experimental conditions, and changing of the properties has related with the forming of surface films with different chemical composition.

Acknowledgments
This work has been supported by the Russian Foundation for Basic Research (project no № 18-01-00513_A). A part of investigations has been carried out on the equipment from the Core Facility Centre in Derzhavin Tambov State University. Facilities (XPS) of the Krasnoyarsk Regional Research Equipment Centre of SB RAS were employed in the work.

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