

VARIATION OF THE PHASE AND STRUCTURAL STATE OF ÉP-838
AND 316SS ALLOYS IN INTERACTION WITH HYDROGEN

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Sections of the plasma chamber (the first wall) of the thermonuclear reactor (TNR) must be made of materials resistant to hydrogen embrittlement and radiation swelling. To reduce the extent of hydrogen embrittlement, it is essential to achieve low values of the diffusion parameters of hydrogen in the first wall material. This also solves the problem of preventing leakage of hydrogen and its isotopes into the environment [1].

The vacancy swelling susceptibility of structural materials is determined by the phase and structural state [2]. The main method of reducing the extent of vacancy swelling of the alloys is to intensify, by alloying, the processes of the type of ordering, phase separation, formation of the K-state etc. [3, 4]. These methods result in the formation of additional interphase boundaries acting as sinks for excess vacancies. Since hydrogen penetrates into the crystal lattice of the metal, changes its electron structure and, consequently, reduces the intensity of the interatomic interaction and, in the final analysis, accelerates self-diffusion, atomic ordering, and diffusion of the solute [5-7], it is of great interest to examine the special features of breakdown of the solid solution in the presence of interstitial hydrogen.

The aim of this work was to examine the effect of hydrogen on the kinetics of phase and structural transformations in ÉP-838 ($10\text{Kh}12\text{G}13\text{N}5\text{M}2\text{Yu}$) and 316SS (Soviet analog $06\text{Kh}17\text{N}12\text{M}2\text{GS}$) alloys. These alloys are extremely promising materials for the first wall of the thermonuclear reactor. To solve this task, we use the methods of electrical conductivity, hydrogen permeability, and x-ray diffraction analysis. The diffusion coefficient D and hydrogen permeability P were determined in volumetric equipment using a MacLeod automated pressure gage [8]. The hydrogen solubility S was calculated on the basis of the results using the equation $S = P/D$ [9]. The phase and structural state of the alloys was examined by the x-ray diffraction method in DRON-2.0 equipment ($\text{FeK}\alpha$ radiation). The temperature and time dependencies of the variation of electrical resistivity were recorded using an automatic ac compensator [10]. The hydrogen pressure in all the experiments was 10^5 Pa.

It should be mentioned that the temperature (in the range 573-973°K) dependences of hydrogen permeability, diffusion coefficient, and hydrogen solubility [11, 12] contain no inflection points or breaks. However, since these alloys are of the multicomponent type, it should be expected that the short-range atomic order will form in them. We believe that the absence of this order was caused by the narrow temperature measurement range. In addition to this, the efficiency of detection of the signs of atomic ordering is improved by stimulating isothermal annealing providing additional information of the phase and structural changes in the alloys and on the effect of hydrogen on them. The main special feature of the investigations carried out in this work (Fig. 1, Table 1) is that to determine the possibilities of occurrence of ordering or breakdown of the solid solution, the measurement range was widened towards higher temperatures (to 1173°K) and a series of isothermal annealing tests with the simultaneous evaluation of hydrogen permeability was carried out.

The temperature dependences of the diffusion parameters P , D , and S for 316SS steel (Fig. 1a) are described by the Arrhenius straight line indicating that no phase transitions take place at these temperatures. The small difference in the absolute values of D and S obtained in the present work and those published in literature [11] can be explained by the effect of oxide films studied in the present work. After isothermal annealing 316SS steel

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TABLE 1

Alloy	T, K	Diffusion parameters of hydrogen						Source
		P_0 , mole/m ³ · sec·Pa ^{1/2}	E_p , kJ/ mole	D_0 , m ² /sec	E_D , kJ/ mole	S_0 , mole/ m ³ · Pa ^{1/2}	H_S , kJ/mole	
316SS	1113...673	$3,40 \cdot 10^{-7}$	62,4	—	—	—	—	[12]
316SS	1073...673	$4,47 \cdot 10^{-7}$	64,5	—	—	—	—	[12]
316SS	1018...413	$2,35 \cdot 10^{-7}$	62,7	—	—	—	—	[12]
316SS	873...573	$4,80 \cdot 10^{-7}$	64,1	—	—	—	—	[12]
316SS	923...623	$1,16 \cdot 10^{-7}$	61,9	$4,15 \cdot 10^{-7}$	53,1	0,28	8,88	[11]
316SS	1173...573	$2,73 \cdot 10^{-7}$	66,4	$1,98 \cdot 10^{-6}$	37,1	0,14	29,30	*
EP-838	973...573	$1,67 \cdot 10^{-7}$	66,5	$2,86 \cdot 10^{-7}$	54,1	0,58	12,40	[11]
EP-838	973...573	$1,55 \cdot 10^{-7}$	69,7	$3,90 \cdot 10^{-7}$	42,1	0,40	27,90	*
EP-838	1173...973	$9,55 \cdot 10^{-7}$	79,4	$3,90 \cdot 10^{-7}$	42,1	2,40	37,30	*

Comment. E_p and E_D are respectively the activation energy of hydrogen permeability and hydrogen diffusion; H_S is the heat of dissolution of hydrogen; P_0 , D_0 , and S_0 are the preexponential multipliers. The asterisk denotes the results obtained in the present work.

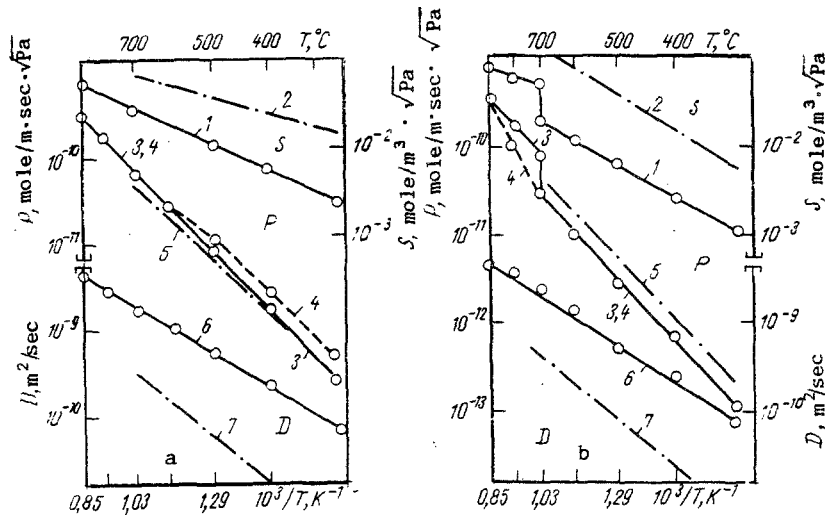


Fig. 1. Diffusion parameters of hydrogen in 316SS (a) and EP-838 (b) alloys: 1, 2) solubility; 3, 4, 5) hydrogen permeability; 6, 7) hydrogen diffusion coefficient (2, 5, 7, according to the literature data [11]).

at temperatures of 573, 673, and 773°K for 3 h, the hydrogen permeability increases (Fig. 1a, curve 4) while the activation energy of the process remains almost unchanged (curves 3 and 4). Since the increase of the annealing temperature does not cause changes of this type, this indicates that atomic ordering with the formation of the short-range "local" order (K-state) takes place [13]. In all likelihood, the appearance of the maximum of electrical resistivity during isothermal holding at 673°K for 5 h (Fig. 2a) is associated with the precipitation of the particles of the ordered phase [14] with conduction electrons additionally scattered at the boundaries of these particles. The height of the maximum of electrical resistivity and the area delineated by this maximum are proportional to the amount of secondary phases.

The widening of the temperature range of measurement of the diffusion parameters of hydrogen in EP-838 alloy showed that a phase transition takes place at 985°K; this is reflected in a "jump" of hydrogen permeability and solubility (see Fig. 1b). This type of variation, confirming that the phase transitions of the first kind are completed in the alloy [15], can be determined either by atomic ordering or polymorphous transition. However, in the $\alpha \rightarrow \gamma$ transition in pure iron the hydrogen permeability decreases instead of increasing [13]. In addition to this, the hydrogen diffusion coefficient does not change in the examined temperature range. At present, this is difficult to explain on the basis of the theory of atomic ordering in the presence of an interstitial solute [15], although the disagreement between the temperature dependences of hydrogen permeability in heating (curve 4)

TABLE 2

Alloy	Lat-tice type	Vacuum an-nealing		Hydrogen annealing	
		<i>hkl</i>	<i>d</i> , n. nm	<i>hkl</i>	<i>d</i> , n. nm
EP-838	fcc	222	0,10376	222	0,10404
	fcc	311	0,10839	311	0,10867
	fcc	220	0,12729	220	0,12710
	fcc	200	0,18028	200	0,18003
	fcc	111	0,20766	111	0,20735
	bcc	—	—	110	0,20300
316SS	fcc	222	0,10383	—	—
	fcc	—	—	311	0,10843
	fcc	220	0,12720	220	0,12710
	fcc	200	0,17940	200	0,18003
	fcc	111	0,20714	111	0,20735

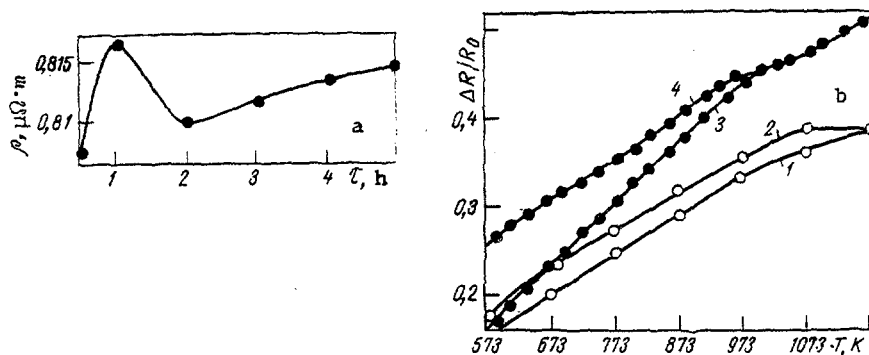


Fig. 2. Variation of specific electrical resistivity of 316SS alloy (a) and the temperature dependence of the electrical resistivity of EP-838 alloy (b) in vacuum (1, 2) and hydrogen (3, 4).

and cooling (curve 3) indicates that microregions can form [16] in which the atoms of one type are surrounded mainly by the atoms of another type (positive order or short-range ordering), or by the atoms of the same type (the negative short-range order or short-range delamination) [17]. According to the literature data on the interaction of hydrogen with the elements included in the alloy, and the binary compounds produced on the basis of these elements, the polymorphous $\alpha \rightarrow \beta$ transformation in iron-manganese (more than 40 at. %) alloys is the most similar type of transformation as regards the qualitative changes of the diffusion parameters of hydrogen and phase transition temperatures [18-20]. However, since the manganese concentration of the alloy is lower (14 at. %), it was assumed that at high temperatures the solid solution breaks down with the precipitation of secondary phases enriched with the element. It is evident that the manganese content of the microregions changes in wide ranges and this widens the temperature range of the transformation ("scattering" of the jump in curve 4) and leads to fracture. In addition to this, isothermal annealing at 985°K reduces hydrogen permeability. This can also be attributed to the secondary phases.

To verify this assumption, we examined the temperature dependences of the electrical resistivity of EP-838 alloy in vacuum and hydrogen (Fig. 2b). In measurements taken in vacuum the anomalies caused by the phase transition were not detected. The structural hysteresis in heating (curve 1) and cooling (curve 2) is caused by excess thermal vacancies which do not manage to recombine with decreasing temperature [21]. After supplying hydrogen (curve 3) the electrical resistivity of the alloy increases. This can be explained [19] by the increase of the lattice parameter in absorption of hydrogen by the precipitates of the second phase enriched with manganese. Therefore, we believe that the jump of the electrical resistivity at 985°K coinciding with the identical anomaly of hydrogen permeability and not occurring in vacuum is the result of the variation of the hydrogen concentration of the iron-manganese microregions. The reduction of the temperature of formation of the structural hysteresis in hydrogen to the region of the $\alpha \rightarrow \beta$ transformation indicates that the migration of the vacancies in the metallic matrix becomes easier and, consequently, the rate of recombination of the vacancies increases [5]. Thus, the measurements of the electrical resistivity of EP-838 alloy, on the one hand, confirm the results of examination of the diffusion

parameters of hydrogen and, on the other hand, the problem of the identification of the phases and variation of the initial structure of the metal under the effect of hydrogen has not been solved by these measurements.

Since manganese widens the range of existence of the γ -phase of iron [22], the generation of microvolumes enriched with this element, leading to depletion of the metallic matrix in this element, creates suitable conditions for the formation of α -phase in EP-838 austenitic alloy. However, the unambiguous determination of the structure of the phases is complicated both by the similarity of the atom factors of scattering of the main components of the alloy and by the relatively small volume and fine dispersion of the second phase. Therefore, we examined the specimens subjected to sensitizing annealing at 673°K in vacuum and hydrogen.

The diffraction patterns of the specimens of EP-838 alloy annealed in vacuum for 5 h correspond to the solid solution of the alloying elements in γ -iron. This is indicated by only the small change of the position of the lines in comparison with the line of pure iron (fcc structure). The diffraction patterns contain no special features (Table 2) which would confirm the formation of the individual phases. Identical heat treatment in hydrogen widens the lines of γ -iron, i.e., it leads to the development of concentration heterogeneities in the solid solution [23]. The additional diffraction maxima identified as the reflection from the (110) plane of the bcc lattice of α -iron confirm the assumption on the physical nature of the second phase. The fact that the α -phase of iron in the austenitic matrix of EP-838 alloy forms in hydrogen and does not form in vacuum at the same annealing time indicates, we believe, that the precipitation of the secondary phases is stimulated by dissolved hydrogen. In 316SS steel heat treatment results in slight texturing of the specimens changing the relative intensity of the reflections. After annealing in hydrogen, the reflection from the (222) plane disappears and the new line (311) appears. However, the α -phase of iron was not detected in the heat treated 316SS alloy.

On the basis of the investigations it can be concluded that high-rate processes of atomic ordering with the formation of the short-range atomic order increasing hydrogen permeability take place in 316SS steel in the temperature range 573-773°K. Therefore, EP-838 alloy is more efficient in minimizing the leakage of hydrogen and its isotopes through the first wall of the thermonuclear reactor. The flow rate of hydrogen through this alloy can be controlled by heat treatment in the phase transition temperature range by varying the kinetics of precipitation of manganese-enriched secondary phases.

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A METHOD OF EXAMINING THE HYDROGEN PERMEABILITY OF PASSIVATING FILMS ON METALS

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It is well known [1] that the passivating films (PF) act as barriers in the path of penetration of hydrogen from electrolytes into metals. However, there are only a small number of quantitative data on hydrogen permeability (HP) of the films. For example, it is not clear whether the barrier properties of the PFs are determined by the low diffusibility of hydrogen or by inhibition of the discharge of the hydrogen ions on the PFs. There are different views regarding the possibilities of formation of PFs in active dissolution of the metals. The aim of this work was to develop a method of examining the hydrogen permeability of the passivating films by modifying the method of measuring this permeability through metallic membranes [2].

In most cases, the conventional method uses thick (≥ 0.7 mm) membranes to level the effect of the surface processes, especially the PFs, and also the high densities of cathodic currents and hydrogen charging accelerators. The proposed method is based on the use of a membrane of minimum thickness for levelling the role of hydrogen diffusion in metal and ensuring the operating regime with the maximum extent of surface inspection on the cathode side of the membrane. For example, at a membrane thickness of 10-20 μm made of Armco iron, the diffusion penetration time of hydrogen is 0.01-0.1 sec. Taking into account the rapid (several microseconds) establishment of the equilibrium (at the given potential) degree of filling the surface with adsorbed hydrogen [1], any delay of HP through such a membrane exceeding 0.1-1 sec should be explained by surface control, i.e., HP of PF. Difference between the values of the stationary flows of hydrogen through the membrane with increasing and decreasing potential also provides information on HP of PF and the kinetics of their formation and failure.

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