

Study of the Dynamics of Hydrogen Accumulation in 12H12M1BFR Steel¹

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Abstract – Studying the accumulation of hydrogen under the electrolytic saturation showed that the speed of accumulation of hydrogen under times of saturations more than 50 h reduce; a common amount of absorbed hydrogen is stabilized. Under times of saturations less than 50 h the amount of introduced hydrogen linearly grows with saturation time, and the temperature spectrum of hydrogen discharge changed the position, under these changes spectrum maybe interpreted in the next sample. In the beginning there is a capture of hydrogen at low-temperature (400–500 °C) the traps of several types, located at the surface. And only at times of saturation of 48 h and more hydrogen penetrates to high-temperature (800–900 °C) to the traps which located more deeply under the surface layers.

1. Introduction

It is impossible to use 12H12M1BFR ferrite steel, in the applications of the capacity of constructional devices, in the active parts of atomic reactors, without in-depth study of the mechanism and kinetics of the processes which occur in a corrosive environment under the effect of an irradiation and stress. Materials of nuclear energy, Containers for a storage and transportation of radioactive materials should satisfy extreme requirements to maintain radiation safety. Accumulation of hydrogen is one of the most considerable reasons of degradation of technological properties in these materials, which gives rise to embrittlement and a drop of plasticity, especially in the regions of welded joints. Penetration of hydrogen into steel significantly depends on the requirements of its implementation. In the present work the effects of electrochemical saturation process on dynamic of hydrogen accumulation is investigated.

The motion of hydrogen and its accumulation in the sample stimulate diffusion of defects, impurity atoms and conduct to the rearrangement of the defect structure of materials. Enumerated, as it will be visible from the subsequent, it is reflected in the temperature spectra that thermo-stimulated gas extraction (TSGE) (more spread title is thermo-stimulated desorption (TSD) method).

2. Materials and experimental techniques

Samples of ferrite steel mark 12H12M1BFR have been manufactured from a sheet of material by a method of spark cutting in rectangular plates with sizes 25×5.0×2.0 mm.

For removal of the defected surface layers, samples have been mechanically grounded and polished. All samples were annealed in an evacuated furnace at temperature 750 °C within 1 h with subsequent cooling in furnace without disturbance of the vacuum.

Saturation of samples with hydrogen was carried out in an electrolytic cell from 1M solutions H₂SO₄ with ordinary or heavy water at a current density of 0.5 A/cm² and time of saturation from 2 to 74 h. Dynamic of accumulation of hydrogen was investigated by means of an entry, comparisons and analysis of temperature spectra TSGE during the linear heating after different times of samples saturations. Further temperature spectra were integrated and constructed depending on an integrated yield of hydrogen at the time of saturation.

The entry of spectra TSGE of hydrogen at thermo-stimulated discharge of gas was carried out with the help of a complex hardware-software, which enabled the controlling of the display of mass spectrometer MX-7304, to produce a linear heating of samples and recording in a file, the values of temperature and intensities of the selected lines of a mass spectrum (from 1 up to 6) with a speed from 1 till 10 measured in seconds. Final treatment of observed data was produced with the help of a package of applied programs OriginPro 7.0 (OriginLab computation). More details about the procedure of measuring and analysis see in [2, 3].

For evaluation of hydrogen binding energy in traps was used the method based on calibration covers of the dependence of desorption activation energy E_d on temperature $T_{\max,i}$, at which observed the maximum in the dependence of hydrogen release on the temperature and heating rate [3, 4]. Using the given relations and taking into account the small difference between binding energy of hydrogen atoms in the sample E_b and desorption activation energy E_d , it is possible from the evident image use the given relations for evaluating E_b .

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3. The experimental results and discussion

During linear heating of samples traced spectra TSGE for the following masses: 1 (H), 2 (H_2), (DH), 4 a.m.u. (D_2), 13 (CH), and 17 a.m.u. (OH). The Mass of D_2 was traced only after saturation in a heavy water. Comparison of intensities of the enumerated masses after saturation in electrolytes on the basis of heavy and ordinary water reveals that in both cases the most intensive mass in all spectra TSGE is OH.

The difference is that after saturation in the electrolyte on the basis of heavy water the spectra showed that there are masses of DH and D_2 , which was provided by integral (by spectrum TSGE) intensities from 2 to 3 times lower than the intensities of OH and H_2 .

It gives evidence that the mode of processing samples before saturation prevails over the influence on samples under the action of an electrolyte during saturation. Fig. 1 shows the spectra TSGE of H_2 after saturation in light and heavy water.

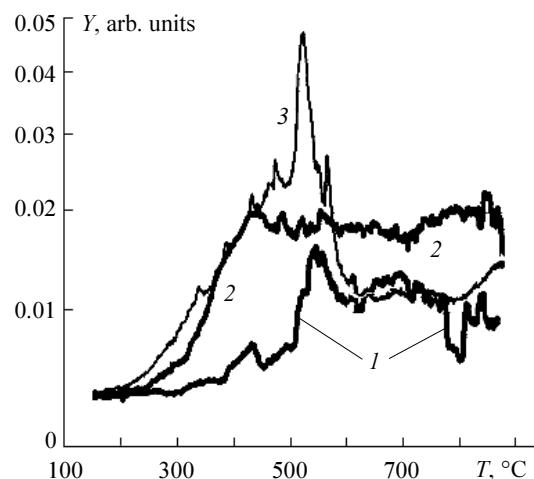


Fig. 1. TSGE H_2 from steel 12Х12М1БФР after saturation in heavy (2) and ordinary (3) water: 1 – an initial sample; 2, 3 – after 12 h of saturation

It is observed that an integrated release is practically equal, but after an electrolyte in the basis of ordinary water in an indicated time of saturation, the spectrum appears narrow peak near 500 °C (hydrogen binding energy $E_b \sim 1.5$ eV). After a long times of saturation this peak disappears, as shown in Fig. 2.

In Fig. 2, spectra TSGE of hydrogen H_2 from steel 12H12M1BFR for various times of the electrolytic saturation are reduced. It is shown, that in due course saturations all over again (after time of saturation of 12 h) there is a peak of hydrogen at a temperature of ~500 °C. By increasing the time of saturation till 24 h this peak moved in the range of 400–500 °C and broadens (hydrogen is captured on traps with a binding energy $E_b \sim 1.2$ –1.5 eV). With a further increase with the time of saturation (till 48 h, curve 5) grows up intensity of peak in the range of 400–500 °C and shows a peak nearly at 900 °C (hydrogen is captured on traps with a binding energy $E_b \sim 2.4$ –2.6 eV). And

with a more further increasing of the time of saturation (measured at 64 and 72 h) the general pattern of spectrum and the total intensity of peaks Fig. 2 does not change, originate only a relative oscillations of the intensities of peaks, that, apparently, related to lapses in the sample preparation.

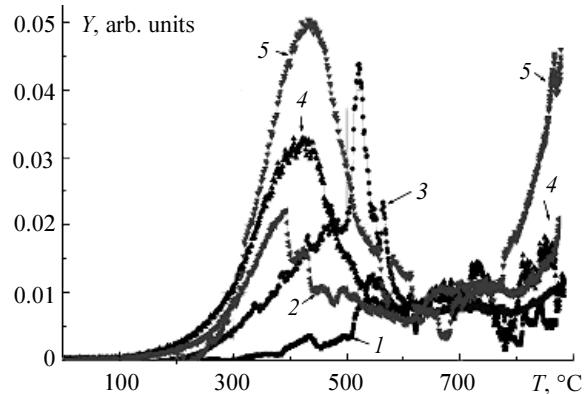


Fig. 2. Spectra TSGE of hydrogen H_2 from steel 12Х12М1БФР after different times of saturation (t , h): 1 – an initial sample; 2 – 6; 3 – 12; 4 – 24; 5 – 48 h. Saturation current density 0,5 A/cm². Electrolyte – 1M H_2SO_4

The indicated behavior of maximum spectra lines TSDE H_2 depending on saturation time specifies on one side the change of hydrogen binding energy in metal, and on the other side the appearance of high temperature traps at times of saturation equals to or greater than 48 h in samples.

It is carried out that before studying of accumulation of hydrogen by secondary ion mass-spectrometry method [5, 6], hydrogen implanted at electrochemical saturation is proportioned extremely non uniformly on the depth of sample: its concentration increased near the surface layer. Therefore the appearance of high-temperature traps is logic for connecting with penetration of hydrogen at a long times of saturation in volume of a sample. Fig. 3 showed the relation between integrated emission of hydrogen at different times of saturation.

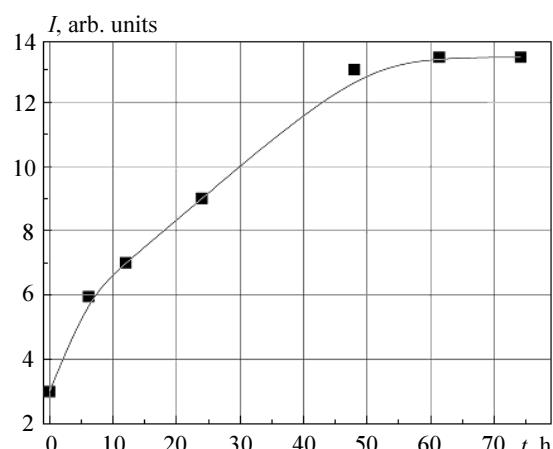


Fig. 3. Dependence of an integral migration of hydrogen H_2 on the time of saturation according to integration of spectra Fig. 2

And it is clear that the relation is practically linear up to ~ 50 h saturation time, after that saturation began. Except for that, it is clear that the total of the maximum emission is 6 to 7 times higher than the emission from the initial sample (under Pb, Ti, and Zn analogous relation maybe in the order of 3–5 [7]). Connecting with results given from Fig. 2, it maybe related in one side to existing of large content of hydrogen in initial samples, which are not deleted at the annealing temperature and during samples preparation, in other side, at a small concentration high-temperature traps, in which hydrogen is captured during long time of saturations.

Samples after 48 h of saturation (see Fig. 2) were irradiated with X-rays with energy 120 keV for one h under the conditions of atmosphere. The effects of such radiation on peak in the range of 400–500 °C is not observed, at the same time, the peak in the range of 800–900 °C possess tendency to insignificant decrease. That is, the atmosphere interrupt with radiation effect on the surface-trapping centers whereas volumetric to such affecting are subject aside.

4. Conclusion

Studying the accumulation of hydrogen under the electrolytic saturation showed that the speed of accumulation of hydrogen under times of saturations more than 50 h reduce; a common amount of absorbed hydrogen is stabilized. Under times of saturations less than 50 h the amount of introduced hydrogen linearly grows with saturation time, and the temperature spectrum of hydrogen discharge changed the position, under these changes spectrum maybe interpreted in the next sample.

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on traps $E_b \sim 1.2\text{--}1.5$ eV). And only at times of saturation of 48 h and more hydrogen penetrates to high-temperature (800–900 °C) to the traps which located more deeply under the surface layers (hydrogen binding energy on traps $E_b \sim 2.4\text{--}2.6$ eV).

Irradiation of hydrogen saturated samples 12H12M1BFR ferrite steel by X-rays shows, that X-rays with energy 120 keV for one h under the conditions of atmosphere deletes hydrogen from high-temperature (volumetric) traps in inappreciable quantity, but on the surface hydrogen does not influence in any way.

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