# The Study of Thermally Stimulated Hydrogen Evolution from Steels by Thermal Desorption Mass Spectrometry Technique

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The hydrogen removal from electrolytically hydrogenated samples of two different steels (ferritic and austenitic) was experimentally studied. The temperature dependences of hydrogen evolution were obtained using the set-up with hot vacuum extraction and mass spectrometric registration of the volatile components. For both steels, the process of hydrogen evolution can be described as consisting of two stages, which are overlapped with different degrees of resolution. In assumption that each moiety is related to a certain form of hydrogen in material (specific trapping site), the kinetic parameters of the process of the gas extraction were estimated for two stages of both samples. The similarity of the kinetic parameters of the first stage indicates the same form (or location) of hydrogen in both steel samples. This is believed to be surface localized hydrogen. The kinetic parameters of the second ("high temperature") stage have more significant differences, which may indicate different kinetics of the thermally stimulated removal of hydrogen from the near-surface layers of $\alpha$-Fe and $\gamma$-Fe. These parameters can serve as markers of the localization of hydrogen in various steels and allow one to compare the ratios of different forms of hydrogen in such materials.

**Keywords:** Hydrogen, Steel, Thermal desorption mass spectrometry, Kinetic parameters, Hydrogen thermal extraction.

## 1. INTRODUCTION

The hydrogen in metals and related problems are constantly under the close attention of specialists in physical materials science. At certain concentrations of hydrogen, mechanical and thermal stresses, metal structures are subject to destruction due to hydrogen embrittlement. Radiation damages created in nuclear power plants, in which large amounts of hydrogen and helium are generated, can contribute to the trapping and accumulation of hydrogen, with its subsequent effect on the development of radiation porosity, embrittlement, corrosion and cracking [e.g., 1-3]. Since the life time of nuclear materials is determined by the content of accumulated hydrogen, it is necessary to control both its total concentration and the relative amount of hydrogen, which can be in different states: in solid solution, in the form of hydrides, in the form of gas porosity, trapped in defects, and in the secondary phases [2, 3].

The method of thermal desorption mass spectrometry (TDMS) was widely used to study hydrogen (helium) isotope in metals by observing desorbed gas molecules from the near-surface region of solids when the sample temperature is increased [4-7]. This method is applied to determine both the integral content of the gas-forming impurity, and the activation energy associated with each detrapping event. In the latter case, the accuracy of the calculations is determined by the thickness of the analyzed layer; therefore, thin films or coatings are used for measurements. This is due to the fact that in bulk samples as the temperature rises, impurity atoms have the option not to leave the sample, but pass from low-energy states to vacant high-energy bound states. Therefore, the applicability of this method for the metal-hydrogen systems is limited to surface and partly near-surface ($\leq$ 200-500 nm) regions.

A reasonable model of hydrogen-saturated metal are electrolytically hydrogenated thin plates. To date, a great deal of experience has been accumulated in both the method of hydrogenation and the interpretation of thermal desorption spectra. The hydrogen distribution profiles were studied by the SIMS method, and its predominantly surface localization was established [3]. At the same time, in applied research of materials for nuclear power for comparative assessment of trapped hydrogen in different locations, it is necessary to have information on the quantitative parameters of hydrogen and helium thermally stimulated evolution.

The aim of this work was to determine the temperature range and quantitative characteristics of thermostimulated hydrogen evolution from two samples of different steels (ferritic and austenitic), subjected to electrolytic charging by hydrogen. Experimental data were obtained by non-commercial set-up with hot vacuum extraction and mass spectrometric monitoring of the volatile components.
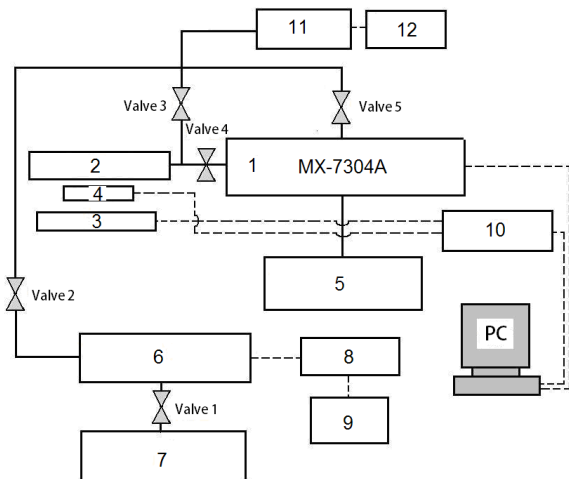
## 2. MATERIALS AND METHODS

Two different samples of steel were offered for study: (1) carbon steel and (2) high-alloy corrosion resistant steel. The structural characteristics of the samples were studied by X-ray diffraction using the diffractometer DRON4-07 ("Burevestnik", Russia) connected to the computer-aided experiment control and data processing system.

The temperature dependences of hydrogen evolution were obtained using a hot vacuum temperature

extraction set-up (Fig. 1) with mass spectrometric registration of the volatile components (MX-7304A, SELMI, Sumy, Ukraine).

The method is based on the fact that at a constant pumping rate, the gas pressure in the pumped-out volume is proportional to the rate of gas evolution from the test material. The sample was heated in an evacuated quartz tube (the initial vacuum was $3 \times 10^{-2}$ Pa) at a constant rate of 15 °C/min up to 900 °C while simultaneously recording the mass spectra of the extracted gases. This offered to determine the temperature intervals of the gas outlet, the variation of the intensity of the released gas as a function of temperature and, ultimately, to estimate the kinetic parameters of the process. To control the heating regimes of a high-temperature furnace and a mass spectrometer, as well as for recording and processing data, we used a special software package of our own design. The technical details of the setup and the TDMS experiment are described in more detail in [8].



**Fig. 1** – Set-up of thermal desorption mass spectrometry (TDMS): 1 – mass spectrometer; 2 – evacuated quartz tube with a sample; 3 – furnace (1200 °C); 4 – thermocouple; 5 – magnetic discharge pump; 6 – turbomolecular pump; 7 – fore-vacuum-smart pump; 8 and 11 – vacuum sensor; 9 and 12 – vacuum gauges; 10 – furnace control unit

Before TDMS studies, steel samples (in the form of plates of $20 \times 8 \times 2$ mm) were charged by hydrogen in an electrolytic cell. The electrolysis was carried out in a 1 M $H_2SO_4$ water solution at a current density of $5 \cdot 10^3$ A/m². Saturation time was 6 h; processing temperature was 20 °C; the time interval between the removal of the sample from the electrolytic cell and the beginning of the TDMS measurement was at least 2 h.

TDMS studies began with the registration of all gases released from the hydrogenated steel sample upon heating. The obtained mass spectra contain the peaks of ions with molecular masses (*m/z*): 2 – hydrogen ($H_2$), 18 – water ($H_2O$), 28 – carbon monoxide (CO) and 44 – carbon dioxide ($CO_2$). The most intense signals were recorded in the low-temperature region (up to 300 °C), which correspond mainly to the release of water. In the high-temperature region (500-900 °C), CO and $CO_2$ prevail among the released gases. The temperature range of molecular hydrogen evolution lies within 40-450 °C, although at higher temperatures (550-850 °C) the signal of

$m/z = 2$ slightly rises above the background. Control samples not subjected to hydrogen saturation did not show a clear hydrogen evolution in the temperature range 40-450 °C. In the saturated samples with an increase of exposure time from two to six hours, unsystematic increase in the extracted hydrogen intensity was observed.

## 3. CALCULATION OF THE KINETIC PARAMETERS

We assume that the partial pressure of hydrogen in the heated evacuated volume coupled to the mass spectrometer is proportional to the measured ion current of hydrogen, and the equation of the thermally activated hydrogen removal reaction has the form:
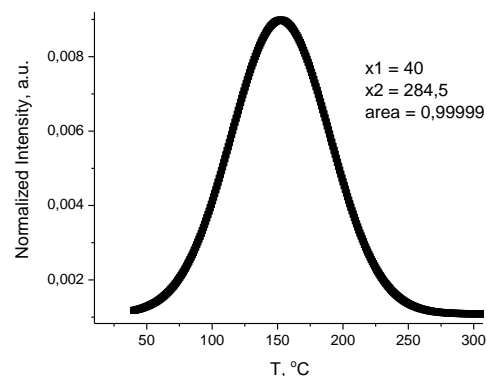
$$d\theta/dt = K \cdot (1 - \theta)^n, \qquad (1)$$

where $K$ is the reaction rate constant; $\theta$ is the normalized amount of all generated hydrogen, variable within $0 \le \theta \le 1$; $t$ is the time; $n$ is the kinetic order of the reaction; for $K$, the Arrhenius formula is valid:

$$K = K_0 \cdot \exp(-E_a/RT), \qquad (2)$$

where $R$ is the universal gas constant, $T$ is the absolute temperature. Kinetic parameters, the pre-exponential factor $K_0$ (frequency factor) and the activation energy of the process $E_a$ characterize a certain form of the presence of the extracted gas in the material.

With increasing temperature, the rate of hydrogen evolution increases, but the degree of filling of the gas source decreases, thus, the temperature dependence of the ion current passes through a maximum – a peak is observed during the TDMS experiment.

Using the OriginPro 9.2 program, we separate the superimposed (unresolved) stages of hydrogen evolution by the multiple peak fit (Gauss approximation) procedure, and then for each component we normalize the area under the "Ion current/temperature" curve per unit. Fig. 2 shows the kinetic curve of hydrogen evolution (ferritic steel, "low temperature" stage) after normalizing the area per unit. In this form, the area under the curve is the total amount of hydrogen released, $\theta$, varying from zero to unity.



**Fig. 2** – Normalized kinetic curve of hydrogen evolution

Integrating the normalized intensity over the interval corresponding to the temperature of hydrogen evolution, we obtain the temperature (or time) function of the fraction of hydrogen released (Fig. 3). The angle of inclination

of the linear part of this curve in the interval of intense hydrogen evolution corresponds to the reaction rate of thermally activated hydrogen evolution (1), in accordance with the chosen kinetic reaction model and for the linear law of temperature change. Thus, in the case of a zero-order reaction $((1 - \theta)^n = 1)$, having the dependence $\ln(d\theta/dt) - 1/T$, we can unambiguously estimate the activation energy of the temperature evolution of hydrogen from the metal $(E_a)$ and the pre-exponential factor $(K_0)$. For reactions of the first and second kinetic orders, the variable factors $(1 - \theta)^{-1}$ and $(1 - \theta)^{-2}$, respectively, are added under the logarithm sign. Reconstructing these dependences from Fig. 3 in the corresponding coordinates, from the graphical data of the linear approximation (Fig. 4) we obtain the numerical values of $E_a$ from the line slope and $K_0$ from intercept of $y$-axis.

Due to the uncertainty in the choice of the kinetic order of the reaction of hydrogen evolution from steel, we determined $E_a$ and $K_0$ for three values of $n$ from 0 to two.
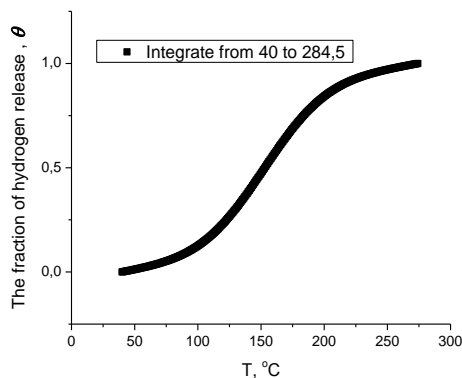


**Fig. 3** – Temperature dependence of the fraction of hydrogen released $(\theta)$
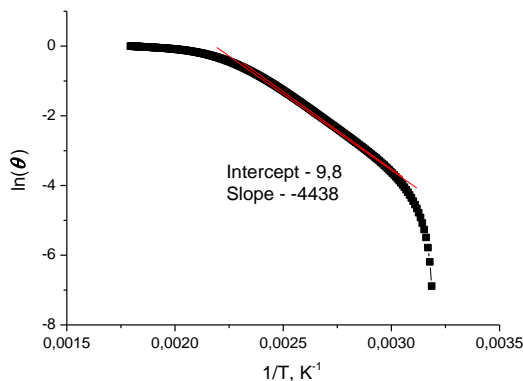


**Fig. 4** – Arrhenius plot for the ferritic steel sample, "low-temperature" stage of hydrogen removal, for the case of a kinetic reaction of zero order

## 4. RESULTS AND DISCUSSION

Fig. 5 shows X-ray diffraction patterns of two steel samples presented for the study. As can be seen, the phase composition of carbon steel corresponds to $\alpha$-Fe (ferrite, body-centered cubic lattice), and high-alloy corrosion resistant steel corresponds to $\gamma$-Fe (austenite, face-centered cubic lattice) with a small amount (8-12 wt. %) of residual ferrite. In this case, the $\gamma$-Fe phase of high-alloy steel is best characterized as austenite of the composition $Cr_{0.19}Fe_{0.7}Ni_{0.11}$ (JCPDS 33-397),

which corresponds to AISI 304 steel. AISI 304 stainless steel is acid resistant and can withstand short-term temperature elevation up to 900 °C. Due to this, AISI 304 steel is widely used in nuclear energy.
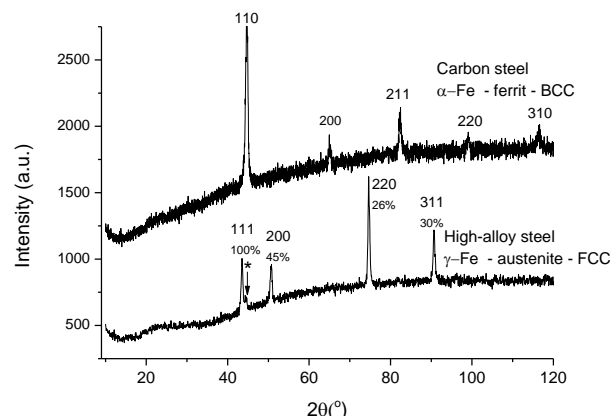


**Fig. 5** – X-ray diffraction patterns of carbon steel of the ferritic class and chromium-nickel steel of the austenitic class; for the latter, relative intensities of the lines of the non-texture standard are indicated under Miller indices, the symbol (*) marks the line 110 of residual ferrite
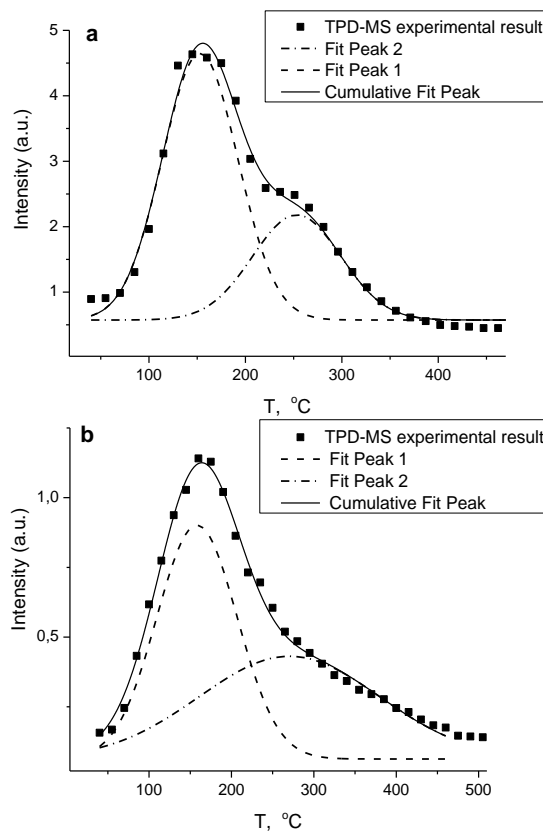




**Fig. 6** – Thermograms illustrating the kinetics of the thermal evolution of hydrogen from samples of steel of ferritic class (a) and chromium-nickel steel of austenitic class (b) subjected to electrolytic saturation with hydrogen

It should be noted that from the X-ray diffraction patterns it is seen that the austenitic steel sample has a pronounced rolling texture with {110} planes lying in the sheet plane ("cube on edge" or "edge texture"), while in the carbon steel sample texture is missing (was delivered in the form of a bar).

Obtained from the processing of the primary mass-spectra, the temperature curves of hydrogen evolution from steel samples subjected to electrolytic saturation are shown in Fig. 6. As can be seen, for both ferritic (a) and austenitic (b) steels, the process of hydrogen evolution can be represented as consisting of two stages, which are superimposed on one another with different degrees of resolution. In order to compare the non-isothermal kinetic parameters of each stage for both samples, we analyzed the obtained thermograms divided into components, as shown in Fig. 6. The similarity (or difference) of the determined parameters, as expected, may indicate the identity (or difference) of the forms of hydrogen in the samples of steel of the ferritic and austenitic class. The results of the calculations for two stages of evolution and three values of the kinetic order of the reaction ($n$) are presented in Table 1.

The similarity of the kinetic parameters of the first peak (stage) indicates the presence of a similar or even identical form of hydrogen in both steel samples. Obviously, this is the hydrogen of surface localization. The kinetic parameters of the second ("high temperature") peak have more significant differences, which may indicate a different kinetics of the thermal removal of hydrogen from the near-surface layers of $\alpha$-Fe and $\gamma$-Fe, taking into account that for hydrogen atoms the most preferred positions in bcc crystals are tetrapores, and octapores in fcc crystals.

As can be seen from the Table 1, with an increase in $n$ from 0 to 2, the values of $E_a$ and $K_0$ increase somewhat, however, the uncertainty of the choice of the kinetic order of the reaction cannot affect the quantitative distinguishability of the kinetic parameters of the two assumed stages of hydrogen evolution from the samples.

The proposed method for calculating $E_a$ and $K_0$ does not pretend to be a method for determining the absolute values of the kinetic parameters of the thermo-activation reactions of hydrogen (deuterium or helium) removal from metals, since it does not rely on a complete process model that takes into account all factors. So, for example, the accuracy of the calculations is determined by the thickness of the analyzed layer,

because as the temperature rises, impurity atoms may not leave the sample, but may transition from low-energy states to free high-energy bound states in its volume. Nevertheless, the proposed approach allows us to distinguish between two (or more) different forms of hydrogen in one sample and to compare their similarity in different samples of similar materials (for example, in steels of different grades).

**Table 1** – Kinetic parameters calculated from the experiment taking into account the two-stage temperature removal of hydrogen from steel samples of two classes

| Stages of hydrogen evolution | $n$ | Kinetic parameters | Ferritic steel | Austen-itic steel |
|---|---|---|---|---|
| Peak 1 (low temperature stage) $T_{max}^{ferr} = 153$ °C $T_{max}^{aust} = 158$ °C | $n = 0$ | $E_a$, kJ/mol | 36.9 | 37.4 |
| | | $K_0$, s$^{-1}$ | $1.8 \cdot 10^4$ | $2.0 \cdot 10^4$ |
| | $n = 1$ | $E_a$, kJ/mol | 45.4 | 46.4 |
| | | $K_0$, s$^{-1}$ | $3.5 \cdot 10^5$ | $4.5 \cdot 10^5$ |
| | $n = 2$ | $E_a$, kJ/mol | 50.2 | 51.6 |
| | | $K_0$, s$^{-1}$ | $2.0 \cdot 10^6$ | $2.9 \cdot 10^6$ |
| Peak 2 (high temperature stage) $T_{max}^{ferr} = 250$ °C $T_{max}^{aust} = 270$ °C | $n = 0$ | $E_a$, kJ/mol | 26.2 | 20.5 |
| | | $K_0$, s$^{-1}$ | $1.9 \cdot 10^2$ | $2.4 \cdot 10$ |
| | $n = 1$ | $E_a$, kJ/mol | 30.1 | 26.8 |
| | | $K_0$, s$^{-1}$ | $6.7 \cdot 10^2$ | $1.3 \cdot 10^2$ |
| | $n = 2$ | $E_a$, kJ/mol | 34.9 | 30.2 |
| | | $K_0$, s$^{-1}$ | $3.0 \cdot 10^3$ | $1.2 \cdot 10^3$ |

## 5. CONCLUSIONS

The kinetic parameters ($E_a$ and $K_0$) of the thermo-activation reaction of hydrogen release determined from the TDMS experiment are a highly sensitive and selective quantitative indicator of the form of its presence in metals. As TDMS spectra may contain several peaks corresponding to well defined desorption processes related to a specific trapping site, the kinetic parameters, determined for each peak, can serve for comparing the localization of hydrogen (deuterium, helium) in various metals and alloys, including reactor steels. From the analysis of thermograms and kinetic parameters, one can not only distinguish two (or more) different forms of hydrogen in a sample, but also compare their similarity in different samples.

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# Дослідження термостимульованого виділення водню зі сталей методом термічно-десорбційної мас-спектрометрії

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Експериментально досліджено кінетику видалення водню з електролітично насичених зразків двох різних класів сталі (феритної і аустенітної). Температурні залежності виділення водню були отримані за допомогою установки вакуумної температурної екстракції з мас-спектрометричною реєстрацією утворених летючих компонент. Для обох марок сталі процес виділення водню можна представити таким, що складається з двох стадій, які накладаються одна на одну з різним ступенем розділення. Припускаючи, що кожна стадія відповідає певній формі присутності водню у матеріалі (специфічному місцю локалізації), кінетичні параметри процесу видалення газу оцінювались для обох стадій двох зразків сталі. Ідентичність/схожість кінетичних параметрів першої стадії вказує на однакову форму знаходження водню в обох зразках сталі. Вбачається/припускається, що це водень поверхневій локалізації. Кінетичні параметри другої («високотемпературної») стадії мають більш суттєві відмінності, що може свідчити про відмінності у кінетиці температурного видалення водню з приповерхневих шарів $\alpha$-Fe і $\gamma$-Fe. Дані параметри можуть слугувати маркерами локалізації водню у різних сталях та давати можливість порівнювати співвідношення різних форм знаходження водню у таких матеріалах.

**Ключові слова**: Водень, Сталь, Термічно-десорбційна мас-спектрометрія, Кінетичні параметри, Температурна екстракція водню.