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Multichannel diffusion vs TDS model on example of energy spectra of bound hydrogen in 34CrNiMo6 steel after a typical heat treatment

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ABSTRACT

The paper is concerned with determination of the energy spectra of hydrogen in steels by the Vacuum Hot Extraction method (VHE). The investigation is performed on example of 34CrNiMo6 steel and the benchmark study of Vacuum Hot Extraction method and Thermal Desorption Spectroscopy (TDS) is provided. The spectrum of the hydrogen binding energy and the hydrogen concentration in samples are identified. Two additional energy levels are found out which are possibly related to strong covalent bonds. An advantage of VHE in comparison with TDS is that VHE approach does not require pre-saturation of samples by hydrogen. It keeps the original structure of the samples and ensures that all types of traps are not destroyed in tests. Additionally, the present approach opens new opportunity of accurate analysis on the base of the model of hydrogen multichannel diffusion in steels.

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Introduction

Ultra high-strength fasteners are important for lightweight design in the field of mobility, such as automotive and rail industry. Such fasteners allow one to reduce both weight and size of combustion engines and to increase their efficiency by increasing the compression in the cylinders. Nowadays some car body parts are made of aluminum alloys. The coefficient of thermal expansion of aluminum is higher than that of steel. Thus only high strength fasteners are able to withstand additional thermal stresses that will arise therefrom. Therefore, high-strength bolts and fasteners are a key element for design and production of lightweight constructions.

High-strength fasteners are usually manufactured from hot-rolled medium-carbon alloy steels. A typical heat treatment involves austenitisation followed by quenching to martensite with subsequent tempering. The ultimate tensile strength of these fasteners is typically between 1000 and 1300 MPa with a yield ratio larger than 0.9, cf. [1].

The delayed fracture susceptibility of 34CrNiMo6 steel was investigated after quenching to martensite with subsequent tempering, see Ref. [2]. It was found that tempering at higher temperatures leads to a sound microstructure with increased resistance to hydrogen embrittlement. The hydrogen measurements were made after tempering and the results indicate a hydrogen content of 0.25–0.3 ppm. Thermal desorption spectroscopy (TDS) (for a description of the methodology, see Ref. [3]) was applied after additional cathodical charging in an aqueous solution of H₂SO₄ for 30 min.

The results of TDS give two different hydrogen binding energies for the samples. After tempering at 400 °C (M400) the measured energy is 12.7 kJ/mol, and after tempering at 520 °C (M520) it is 28.4 kJ/mol. The activation energy of 12.7 kJ/mol corresponds most likely to the hydrogen in the lattice at dislocations and at grain boundaries whereas activation energy of 28.4 kJ/mol is near to the reported value for tempered martensite [4]. All these traps exist in both, M400 and M520, but the tetragonal martensite fraction in M520 is lower. Accordingly [3,4] there have to be two TDS peaks for each sample.

The study of the binding energy of hydrogen carried out in Ref. [2] has a significant drawback. The activation energy of the hydrogen is changed twofold when the tempering temperature changes in 100 °C only. It is difficult to assume that the physical nature of dislocations or the lattice structure is changing so drastically that the binding energy changes twofold. In addition to this, only one peak is observed in TDS, cf. [2]. Hence, the structure of the material changes completely, so that there no longer exist the old type traps for hydrogen in the metal tempered at higher temperatures. Similar discrepancies are observed in other publications where the study was carried out by using the TDS method. For example, in Ref. [5] the binding energy of hydrogen dislocations was specified as 24.1–29.9 kJ/mol and the binding energy of the grain boundaries was shown to lie in the range from 26 kJ/mol to 53.1–58.9 kJ/mol. The ranges of the binding energy of hydrogen traps of different nature are overlapping and it greatly reduces the practical value of the TDS method.

The TDS method is widely used in material science. In practice, all studies of the effect of hydrogen on the structure and properties of metals and non-metals use this method, see e.g. Refs. [6–13]. An important feature of TDS is an independent determination of the binding energy. Under identical conditions (size and shape of the samples, the hydrogen charging conditions etc.) TDS method allows one to trace the influence of sample structure and the concentration of individual alloy components on the value of the binding energy, cf. [12]. However, significant differences appear when we compare data from various researchers.

The influence of various factors on the result of research carried out by TDS method is addressed in a number of papers. For instance, Ref. [14] reports the influence of the sample thickness and the holding time after hydrogen charging on the shape and position of the TDS peak by means of the mathematical modeling. A detailed description and benchmark of the hydrogen charging methods are provided in Ref. [15]. The individual TDS peaks are shown to merge into one peak because of high hydrogen concentrations under charging and it yields only an average value of the energy of hydrogen bonds.

The use of additional assumptions allows one to interpret TDS even in the case in which the test yields a single peak rather than several ones. A Finite-Element modeling of the hydrogen diffusion was reported in Ref. [16] which shows that a single peak of TDS can be accurately and adequately approximated as the hydrogen desorption from two energy levels by adjusting the prescribed diffusion constants and the binding energy values. However, this approach deprives the main advantage of the TDS method which is the possibility of independent determination of the value of the hydrogen binding energy from the test results.

The diffusion process is not taken into account in the TDS equations for binding energies. Regrettably, this fact does not always take into consideration. For example, Ref. [17] suggests the existence of several channels of hydrogen diffusion in the martensitic steels. The present authors have substantiated the existence of such channels earlier in their paper [18,19]. However, all measurements in Ref. [17] were carried out by TDS method.

Regardless of the specific values of the binding energy of hydrogen it is important to know what happens to the hydrogen during annealing and how it changes the energy spectrum since this change demonstrates the predominance of a particular structure creating the hydrogen traps. This information allows one to simulate the behavior of both materials and loaded structures [20–22] and to predict the crack growth, cf. [23,24].

In what follows, M400 (tempered at 400 °C) as well as M520 (tempered at 520 °C) samples are investigated by a different means of hydrogen analysis in order to critically discuss and advance the results described in Ref. [2].

Hydrogen analysis by vacuum hot extraction

An important feature of our study is to measure the natural concentration of hydrogen in the steel samples in contrast to the TDS method applied in Ref. [2] in which the samples had

been specially saturated by hydrogen in the electrolyte solution before measurement of the hydrogen concentration. We have not performed any hydrogen saturation that allowed us to suggest a control of high quality steel products by using our approach.

The initial value of the hydrogen concentration has a strong influence on the mechanical properties of metals and their susceptibility to corrosion and hydrogen embrittlement. So the control of the hydrogen concentration is an important issue during materials' processing, e.g. casting. Advanced hydrogen testing ensures high measurement accuracy and makes it possible to measure very low concentrations in the range of 0.01 ppm.

The present research was carried out by the industrial mass-spectrometric hydrogen analyzer AV-1 that utilizes the Vacuum Hot Extraction (VHE) method [25–28]. The analysis method and the analyzer have been described in Ref. [19] in detail.

The sample preparation system consists of a vacuum extractor and an oven. The sample inside the quartz glass extractor is heated gradually up to an extraction temperature of 400–900 °C. The temperature needed for the analysis is below the melting temperature of the sample. At heating the gases are released into vacuum and analyzed by means of the mass-spectrometer. The time-dependence of the hydrogen flux registered by means of the data acquisition system yields the so-called extraction curve. For analysis of the hydrogen content the cylindrical samples of 8 mm diameter and 10 mm length were machined from annealed steel rods M400 and M520. The extraction curve for M520 samples is shown in Fig. 1.

The area under the extraction curve is proportional to the amount of hydrogen extracted from the sample. By analyzing both the position of the maximum and the shape of the curve one can determine the binding energy, diffusion constants and cumulative volume of the flux which the separate peaks correspond to, cf. [19]. In order to approximate the peak extraction curve we performed the hydrogen diffusion simulation with the different binding energies in samples and applied the multi-channel model of the hydrogen diffusion, see Ref. [19].

For prismatic metal samples of the size (l, a, b) the time-dependence of the total flux $q(t)$ of hydrogen from the sample surface is given by, see Ref. [19]:

$$q(t) = \pi^2 ab l \cdot \left[\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{l^2} \right] \cdot \sum_i C_{0i} \cdot D_{0i} \cdot \exp\left(-\frac{u_i}{kT}\right) \cdot f(t, u_i, D_{0i}), \quad (1)$$

Here function $f(t, u_i, D_{0i})$ is solution of the equation:

$$\begin{aligned} \dot{f} + D_{0i} \cdot \exp\left(-\frac{u_i}{kT}\right) \left(\frac{\pi^2}{a^2} + \frac{\pi^2}{b^2} + \frac{\pi^2}{l^2} \right) f &= 0 \\ f(0, u_i, D_{0i}) &= 1 \\ i &= 1, 2, 3, \dots \end{aligned} \quad (2)$$

at the given values of the parameters: u_i is the activation energy, D_{0i} is the diffusion constant, and C_{0i} denotes the initial hydrogen concentration for the diffusion channels with the number $i = 1, 2, 3, \dots$. For a cylinder sample the dependence $q(t)$ is similar, cf. [18]:

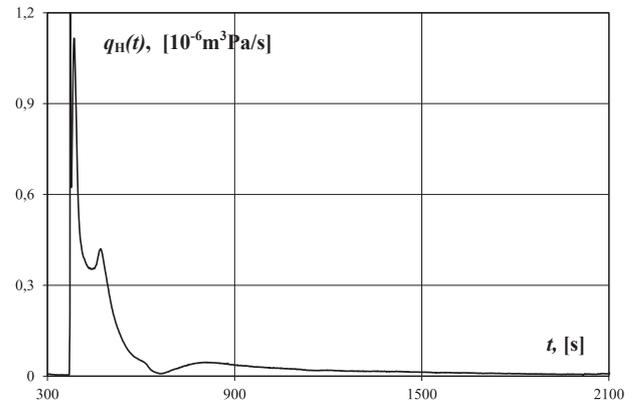


Fig. 1 – Extraction curve for sample M520. Extraction temperature: 900 °C.

$$q(t) = 14.56 \cdot \gamma_1 J_1(\gamma_1) \cdot h \cdot \left[\frac{\pi^2 d^2}{8\gamma_1^2 h^2} + 1 \right] \cdot \sum_i C_{0i} \cdot D_{0i} \cdot \exp\left(-\frac{u_i}{kT}\right) \cdot f(t, u_i, D_{0i}) \quad (3)$$

$$\begin{aligned} \dot{f} + D_{0i} \cdot \exp\left(-\frac{u_i}{kT}\right) \left(\frac{\pi^2}{h^2} + \frac{4\gamma_1^2}{d^2} \right) f &= 0 \\ f(0, u_i, D_{0i}) &= 1 \\ i &= 1, 2, 3, \dots \end{aligned} \quad (4)$$

where h, d stand for the height and the diameter of the cylinder, respectively, and γ_1 denotes the first root of equation $J_0(\gamma_1) = 0$.

Now we can conclude that a certain energy is associated with each peak of the extraction curve as shown in Fig. 2.

In order to approximate the experimental curves the data verification was carried out by extrapolating the simulation results. The diffusion constants u_i, D_{0i} obtained from approximation of the extraction curve with the extraction temperature 900 °C were used to approximate the extraction curves at 400 °C. The result of approximation is shown in Fig. 3 a,b as graphs of both experimental and calculated extraction curves.

The results of extrapolation of the extraction curve to lower extraction temperatures show that the adopted model of multi-channel diffusion does not exactly fit the experimental data. Probably, the process of hydrogen transport was not completely considered. However, the position of peaks on the extraction curve is determined sufficiently accurate and this position is determined by parameters u_i, D_{0i} .

The rate of hydrogen extraction from a sample into vacuum is determined by the sum of the diffusion fluxes in each diffusion channel and each flux depends on the temperature and constants u_i, D_{0i} . We succeeded in approximation of the basis elements of the extraction curves for different extraction temperatures.

Thus, we can talk about a good simulation of the binding energy by using a multi-channel model of diffusion in the samples made of 34CrNiMo6.

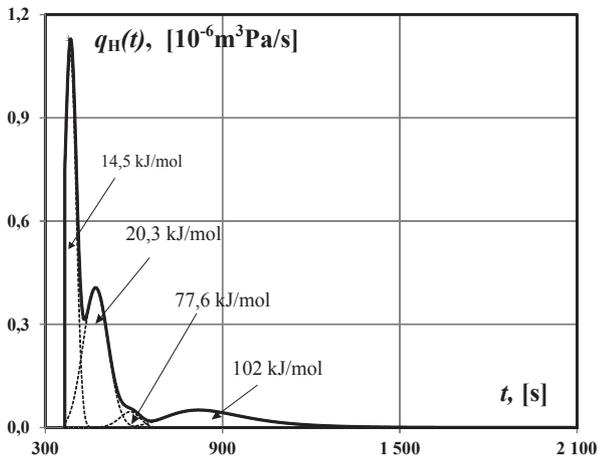


Fig. 2 – Model extraction curve for sample M520 and its peaks with different binding energy. The extraction temperature is 900 °C.

Vacuum hot extraction of tempered 34CrNiMo6

The samples of M400 and M520 were tested at extraction temperatures of 400–900 °C with steps of 100 °C and cooled

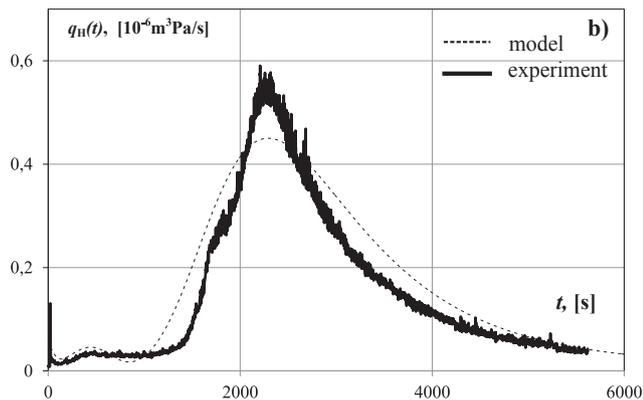
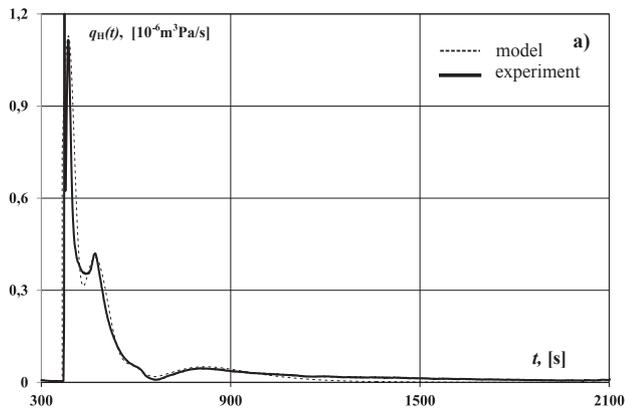


Fig. 3 – Calculated (by the present model) and experimental extraction curve for sample M520 for two values of the extraction temperature: a) The extraction temperature is 900 °C b) The extraction temperature is 400 °C.

after complete degassing at each temperature step. So a set of extraction curves at different extraction temperatures were created, exemplarily shown in Figs. 4 and 5 for 900 °C and 400 °C.

These extraction curves show that the energy spectrum of bound hydrogen in the samples M400 and M520 is exactly the same. This fact has a physical reason. At temperature 900 °C the main peak of extraction curve is well approximated by a multi-diffusion model (see Fig. 3). The presence of small pulses indicates the great influence of the surface hydrogen which is associated with microdefects on the sample surface after lathe treatment (it will be discussed in what follows). The difference in the extraction curves in Fig. 5 is most likely due to the different properties of the sample surface and it is a shortcoming of the method. At low temperatures of about 400 °C the effect of surface processes can be considerable at the hydrogen extraction. They are not described by the diffusion mechanism. It should be mentioned that TDS method is principally not appropriate for correct interpretation of the surface processes since it aggregates them with the processes of internal desorption and hydrogen diffusion.

The total hydrogen content in the sample M400 is 0.22 ppm and in the sample M520 is 0.27 ppm. The full spectra of hydrogen binding energy are given in Table 1.

Practically the entire difference in the initial concentration corresponds to the hydrogen binding energy with the levels lower than 80 kJ/mol.

The binding energies with level 14.5 kJ/mol and 27.3 kJ/mol agree very well with the known data on the binding energies of hydrogen in steels [29,30].

In both samples, the initial concentrations of hydrogen is small, however it was determined experimentally that the higher level of initial concentration leads to lower susceptibility to hydrogen embrittlement [2]. This fact is very well known and is related to irreversible traps with activation energies >60 kJ/mol [31], which make the difference between the initial hydrogen concentrations in the samples M400 and M520. The initial volume of the irreversible traps in M520 is higher than in M400 and these traps lead to a greater resistance to hydrogen embrittlement.

Thus, it appears that the smaller initial volume of the traps with a binding energy of about 80 kJ/mol leads to greater

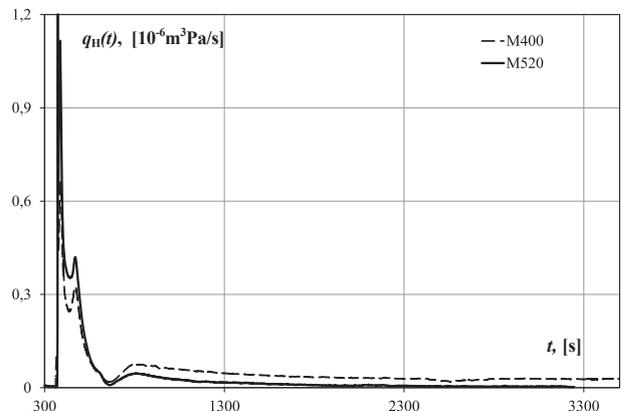


Fig. 4 – Extraction curves for samples M400 and M520 at the extraction temperature of 900 °C.

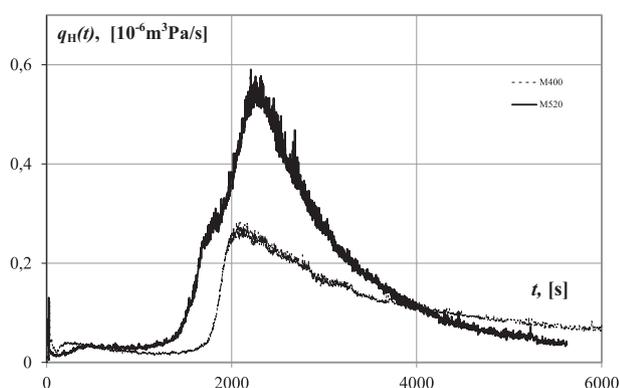


Fig. 5 – Extraction curves for samples M400 and M520 at the extraction temperature of 400 °C.

Table 1 – Values of the hydrogen binding energy in 34CrNiMo6.

#	Hydrogen binding energy	
	kJ/mol	
1	14.5	
2	27.3	
3	77.6	
4	102	

sensitivity of mechanical properties of the steel to hydrogen. It should be noted that this result is difficult to obtain when the samples are saturated by hydrogen because it occurs at the expense of other types of traps; in this case we would obtain the opposite effect, namely the more hydrogen with low binding energy (10–40 kJ/mol) the higher degradation of mechanical properties. Thus, the proposed approach allows us to obtain unique information about the initial state of the material and predict its interaction with hydrogen at saturation.

The role of hydrogen embrittlement is correlated with the high-energy traps. The energy range of 100 kJ/mol is too high to see a significant change in the state of these traps in a short time. Therefore, the outside saturation of the samples which is carried out at TDS measurements is not appropriate for filling these traps uniformly. This level of binding energy of hydrogen was not found out during the investigation by TDS [2]. This is explained by the fact that hydrogen absorption for 30 min is not sufficient to saturate this type of traps and the natural concentrations turn out to be too low (0.04 ppm). As a result, hydrogen saturation results in non-uniform volume distribution of the hydrogen, namely the low energy hydrogen is distributed more uniformly (at high concentrations) in the sample whereas the hydrogen with high binding energy saturates only a thin surface layer of the metal.

In the classical TDS analysis the hydrogen diffusion and the volume distribution of hydrogen are not considered at all. Therefore, the traps with high binding energy which are close to the sample surface do not exhibit any separate peak however these traps significantly displace the hydrogen peaks with low binding energy towards those with higher energies.

These traps may have a strong covalent bond to hydrogen atoms, which could be addressed to sulfur and its compounds [32,33]. Such covalent bonds accompanied by complex

chemical compounds of sulfur and hydrogen have minor influence on the mechanical properties of the metal, however the chemical resistance to corrosion is reduced due to the presence of sulfur.

The difference between the TDS and VHE methods is primarily concerned with the saturation of hydrogen which is necessary for TDS. This saturation does not allow detecting traps with a small capacity limit which may play a role in other types of exposure. The application of VHE however allows gaining additional information about the hydrogen trapping.

It is justified in Refs. [34,35] that for iron it is the dislocations which are the main traps with low energy in the annealed state. However, as pointed out in Ref. [35] this is true for iron with a purity higher than 99.99%.

This issue requires further study for several reasons:

1. The model of the hydrogen extraction from samples under the TDS process was first reported in Ref. [36] however the diffusion of hydrogen in samples was ignored there. Adequate results can only be obtained for thin films. In all other cases a slow heating is used to reduce the influence of the hydrogen diffusion. The increase in the temperature rate causes increasing error. To determine the binding energy it is necessary to use at least three rates of warm-up. The diffusion shifts the spectrum peaks toward greater binding energy under a faster heating.
2. Account for diffusion for TDS method carried out in Refs. [37,38] did not allow one to avoid saturation of samples with hydrogen. This account was performed for only one type of steel and can not be considered as a well established approach.
3. Slow heating at TDS can take dozens of hours, and one must have measured the hydrogen flux from the sample all this time. As a result, the TDS method does not work without special hydrogen saturation. In fact, one measures the distribution of hydrogen traps that can be filled relatively quickly when exposed to the electrolyte or gaseous hydrogen rather than the hydrogen distribution over the binding energies in the sample. Saturation of hydrogen leads not only to a structural change in the spectra of natural hydrogen but also to a substantial change in the mechanical properties of metal itself. Ref. [39] reports the cases of twinning and hence the increase in the traps' volume at hydrogen saturation. Saturating carbon steels with external hydrogen leads to appearance of methane which not only causes the formation of microvoids and cracking (changes in the steel structure) but also absorbs the dissolved hydrogen and changes its energy spectrum, cf. [40].
4. Physical methods of investigation of dislocations and other mechanical imperfections of the crystal structure does not always give a clear quantitative result. For example, Ref. [41] reports that the dislocation density of the specimens was measured by X-ray diffractometry after tensile testing in a hydrogen atmosphere. It was found that all the hydrogen absorbed by high-strength low-alloy steel samples is accumulated in dislocations. This conclusion is based on the method of Ref. [42] which measures the amount of dislocations. However, X-ray diffractometry is known to measure the strains. Ref. [42] suggests a formula

for determining the dislocation density according to X-ray diffractometry on the basis of unsubstantiated assumption that the total deformation of the sample is caused by dislocations only.

5. All these factors lead to the fact that the levels of binding energies of hydrogen traps of the same nature have a large deviation. E.g., for steels the binding energy of hydrogen dislocations lies in the range of 26–35 kJ/mol [43], 20–30 kJ/mol [44], 20–60 kJ/mol [45].

Thus, applying the technique of [19] and VHE on the same samples, we were able to determine more energy levels for bound hydrogen than by using TDS [2]. We succeeded in estimating the filling each energy level or each type of traps by natural hydrogen which was inside the metal when it was processed. The absence of procedure of the hydrogen charging has allowed us to keep the original natural structure of samples. The results show that change in the trap volume with binding energy 77.6 kJ/mol occurs at different annealing temperatures. The physical nature of these traps requires additional investigation, but we can use the mechanical models [46–48] for prediction of the material properties.

Influence of defects on hydrogen flux and discussion

The mass-spectrometric hydrogen analyzer AV-1 measures the instantaneous flux of hydrogen from the sample. As shown in Fig. 3b, the extraction curves exhibit a plurality of small peaks that are not observed with the higher temperature extraction, Fig. 3a. The volume of molecular hydrogen that corresponds to these peaks is approximately 10^{-8} – 10^{-9} mm³. The average grain size in the samples is 50 μm. Thus, each small peak can correspond to a single microcrack or dislocation at the surface of the specimen. According to [49] the grain size affects the hydrogen content. Assuming that the surface dislocations and micro-cracks are of the order of grain size, the volume of the small hydrogen peaks corresponds to the volume of one dislocation.

This hypothesis has been verified. Experiments on the distribution of hydrogen diffusion over some specially created lattice defects in silicon monocrystal were carried out by the present authors. The idea was to create some monocrystal internal defects of the size of about 30 μm and compare the results of high-temperature vacuum extraction of hydrogen of the original monocrystal and the monocrystal with the artificially produced defects. An infrared pulse laser with a wavelength of 1024 nm was used for creating defects. The duration of the laser pulse was 12 nss and the energy of one pulse was 2 mJ. Such a laser is usually used for creating chips in optical glass. The coherent infrared radiation of a pulse is focused on a certain point in the glass. The size of the focused spot is about 30 μm. In the focus the energy density is ca. $2 \cdot 10^{15}$ W/m². Such energy density can heat up the substance to ca. 1500 K depending on the coefficient of radiation absorption. In the heat affected zone one can observe a visible chip. The monocrystal silicon plates of the thickness of 0.3 mm were tested. The plates were placed in a parallelepiped made of optical glass. Some other plates (not radiated by the laser) and the

plate with the chips on the surface were cut in prismatic samples of the size 8 mm × 15 mm × 0.3 mm. After that they were placed in vacuum for carrying out the experiments on the hydrogen diffusion. After extraction of the hydrogen with lower binding energy the gas accumulated in the surface defects starts moving and this effect is recorded as a noise which in turn results in the noise in the form of a number of small peaks. These peaks are due to the emission of hydrogen from silicon. For the regular holes these peaks become regularised and increase their sizes, that is, the volume of the extracted hydrogen increases as well. The observed effect can be interpreted as a regularisation of the diffusion caused by a uniform grid of chips on the surface of the sample. So the verification of the hypothesis gives us an opportunity to determine the approximate number of surface microdefects and their average size with the help of the hydrogen analyzer.

Summarizing, the extraction curve shows a lot of noise during constant hydrogen charging and discharging of surface dislocations and micro-cracks. This may indicate that in the investigated steel the main traps are released at a temperature of 400 °C. Additional studies of samples 34CrNiMo6 are needed to clarify this issue.

Conclusions

34CrNiMo6 steel, tempered at 400 °C and 520 °C, was investigated by means of Vacuum Hot Extraction method. This study was performed on the same samples as the study by TDS published earlier.

The spectrum of the hydrogen binding energies and the hydrogen concentration in the samples were identified. Hydrogen flux from the surface defects was measured at 400 °C.

The application of the vacuum hot extraction analysis makes it possible to detect new energy levels, namely at 77.6 kJ/mol and 102 kJ/mol, which can be related to strong covalent bonds.

The increased hydrogen embrittlement resistance at 520 °C tempering condition can be explained by its higher capacity of irreversible hydrogen.

In contrast to TDS our study did not require pre-saturation of samples by hydrogen. This does keep the original structure of the samples and ensures that all types of traps are present in both M400 and M520 samples. Their binding energy does not change, however the total amount of traps depends on the annealing temperature. It was not possible to draw this obvious conclusion from TDS data since TDS provides the researcher with a single binding energy.

The proposed method based on Vacuum Hot Extraction allows one to obtain adequate data on the binding energies and hydrogen concentration. Additional research is needed to determine the nature of these traps.

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