STUDY OF THE DESORPTION PROCESS FROM THE Zr (62) – Ni (38 wt.%) NON-EVAPORABLE GETTER

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The gas desorption process from the Zr (62) – Ni (38 wt.%) non-evaporable getter produced by the calciothermal technology have been studied. The comparison between the thermostimulated desorption spectra of the samples, which had different prehistory, has shown the history-dependent behavior of spectral line profiles. Variations of the partial pressures of gases released from the getter with temperature increased are presented. Hydrogen bond energies in the hydrogen "traps" have been estimated.

INTRODUCTION

The Zr (62) – Ni (38 wt.%) non-evaporable getter, that was prepared by the calciothermal technology [1] and contained Zr_2Ni and ZrNi intermetallids was abled absorb of hydrogen under the 1 Pa pressure and hold it small amounts up to 1200 K [2, 3]. These properties make it possible to suggest given getter for using as hydrogen "traps" in materials whose resistance to brittle fracture caused hydrogen dissolved therein is one of the basic requirements [4].

X-ray structure analysis of the material under examination have showed this getter contained only two Zr_2Ni and ZrNi phases with crystallographic dates agreed with PCPDF database [5]. Difference at lattice parameters ranges within the accuracy of measurements.

Given getter can be used widely as catalyst in many technical process, like waste rocket fuel, solid – silicon production of good quality and a host of compoundings for perfume manufacturing, hydrocarbon hydro – dehydrogeneration, carbonous oxide hydrogeneration [7] and also in electric – chemical generators [8].

Note that all these appliances use in the modern scientific – technology progress.

As such further study of the Zr (62) – Ni (38 wt.%) non-evaporable getter characteristics it is important and of great scientific and practical interest.

SAMPLES AND INVESTIGATION TECHNIQUES

The calciothermal technology allows produce required materials correctly sized, chemically uniformed, it is energy efficiency and mustered by Ukraine industry.

Zirconium concentration in study ingots is determined by chemical analysis and reached ~ 62 wt.%.

Substantival composition of major impurities is reported in Table.

Impurities content, wt. %					
O_2	N_2	C	Ca	Fe	F
0.12	0.011	0.01	0.07	0.1	0.05

Zr and Ni primary compound concentration in study getter are corresponding to the chemical composition to the Zr–Ni master alloy, obtained in Pridneprovsk chemical plant [9].

Technic for the samples preparation included multi - stage grinding of getter ingots to grit sized 0.2…0.6 mm which is then selected individual flake thickness (~ 0.1…0.01 mm) required for the selected research method [10, 11].

To study the desorption process of the Zr (62) – Ni (38 wt.%) non-evaporable getter were used thermally and temperature – programmed desorption (TPD) methods [10, 11].

Apparatus and methods for obtaining of thermal desorption spectrums and TPD are described in [12].

In this study the heating rate of test samples was chosen based on the requirements of high-grade peaks resolution. On the peaks resolution are influenced by various experimental factors: the heating rate and the temperature of the sample heterogeneity, gases pumping speed from the measured cell and others.

In this case the heating rate of the most important, since on the one hand its decreasing give increasing peaks resolution making them more visible on the other – their height is decreasing and may cause some peaks will be separate hardly from the background on the obtained spectrum.

Accordingly the heating rates of the samples were determined from the heating curves and chosen in the range ~ 12…25 K/min.

Made estimate of the error in the determination of the intensity maxima in the obtained spectrum by the TPD – method was ~ 5%.

Selected methods provide an opportunity to obtain the necessary information relating to the nature of the sorbed and desorbed gases and their interactions; allow for assessment of binding energy of hydrogen in its "traps" (E_b) [10], i. e., research and development of new structural materials purposefully and more effectively.

RESULTS AND DISCUSSION

Fig. 1 shows the thermodesorption spectrums total gas release obtained early in [11] with the getter samples had different prehistory to their studies.

The spectrum 1 in Fig. 1 (labeled 1) refers to a sample that had been in contact with air at $1 \cdot 10^5$ Pa and room temperature during one month, didn't get heat treatment, and didn't become saturated with hydrogen.

The spectrum 2 in the same figure describes the sample further annealed at ~ 1200 K during one minute and at pressure below ~ $1 \cdot 10^{-3}$ Pa which provided the necessary activation of the surface.

The view of the thermodesorption spectra shown in Fig. 1 is typical for the materials had before their research of the intensive deformation as is the case in this study.
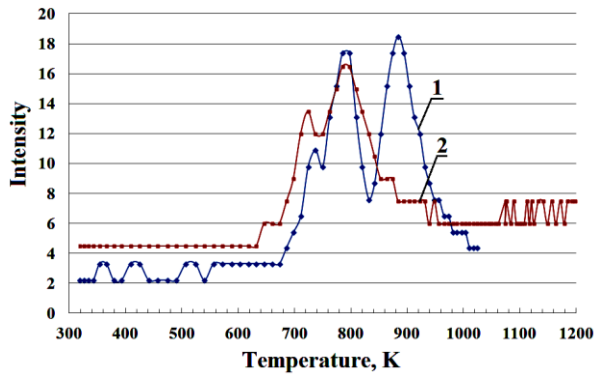

Fig. 1. The thermodesorption of the total gas release obtained getter samples had to study their different prehistory

The presence of each of these spectrums of two distinct maximums, the position on the curves and their amplitudes are explained theoretically and experimentally confirmed in many studies [11, 12].

Comparison of the spectrums presented in Fig. 1 shows the spectrum 2 is dislocated to the spectrum 1 to lower temperature to about 370 K, counting by the shift of the maximum with the greatest amplitude on the curve 1 of the thermal desorption spectrum. Spectrum has become more difficult in the temperature range from 650 K up to temperatures exceeding 1200 K.

Initial position of the spectrum 2 is a straight line shifted by relative intensity scale desorption spectrum 1. Clearly shows the increase (more than 2 – fold) desorption rate from the sample heat-treated.

View the spectrum 1 initial position to a temperature of ~ 530 K was analyzed in [11].

A comparison of the spectra 1 and 2 in Fig. 1 shows that the samples prehistory also affects the view of the thermal desorption spectrum curve. So, most of the points of inflection on the curve 2, relating to the heat-treated steel sample became barely visible, or their position on the curve it is impossible to pinpoint, because they escaped thick graph line.

Plateau on the same curve 2 have arised on those parts of the spectrum, where they previously were not, and those that were changed their length. On the spectrum 2 also have been appeared new maximums, and those that previously observed, changed their amplitude.

In the thermal desorption spectra presented in Fig. 2, showed the changes of partial pressures of all the observed gases (except hydrogen) with masses from 16 to 44, released from the test samples with the increase of temperature from room temperature and up to ~ 1200 K.

Each graph Fig. 2 compares two spectra, taken from samples that had to their research different prehistory, exact, as already reported in the analysis of the thermal desorption spectra in Fig. 1.

All graphs Fig. 2 clearly show that the thermal desorption curves taken from samples subjected to heat treatment are higher, ie of them is more intense gassing.

This fact was the case when comparing the spectra in Fig. 1. This feature of the thermal desorption due to the fact that the heat-treated sample destroyed and largely removed passivated surface layer. Thus, the surface has acquired the ability to more intense as the absorption and release of gas, depending on the conditions under which the sample is.

The knowledge of the partial pressure of the impurity gases can more accurately determine the locations of the maxima in the thermal desorption spectra of the total gas release, and the partial pressure of the impurity gas, and thus pinpoint on the total outgassing spectrum the maximum of hydrogen desorption. The clean atmosphere in the mass spectrometer measuring cell, the lower the hydrogen scattering by impurity gases and fragments thereof, and therefore, it is possible to more accurately determine the maximum desorption temperature. And, hence, more accurately estimate the magnitude of the hydrogen activation energy (E_{act}). And since between this value and the value of the hydrogen binding energy (E_b) in his "traps" is a slight difference, we can use this fact to E_b estimates [9, 10, 13].

Explanation of the partial pressure spectra all desorbed gas, represented in the Fig. 2, especially in the field of high-temperature areas (above ~ 900 K) presents considerable difficulties and may lead to erroneous conclusions. This is due to the fact that the process of thermal desorption gases imposed a number of factors that affect the appearance of the obtained spectra.

First of all, hydrogen thermal desorption from it "traps" with different E_b.

Furthermore, if in the thermal desorption process of the getter material phase transitions occur, as is the case if some of initial getter components have polymorphic transformations [14], this can lead to a significant complexity of the spectrum and its subsequent explanation.

This is because the getter material having various types of defects that their interaction occurs, annealing, etc. This also leads to a complication of the form of the spectra and their interpretation.

It should also be noted that for the type of thermal desorption spectra, particularly their high temperature regions may influence desorption of the vacuum chamber, although this effect was minimized by structural design of used techniques.

Based on the analysis of the spectra presented in Figs. 1 and 2 has been selected maximum corresponding to a temperature of 884.15 K, as such, which is characterized by the most intensive hydrogen desorption, and it choice makes it possible to determine the hydrogen E_{act} most accurately. In addition, the intensities analysis of all gases observed in the spectra

of Fig. 2, shows that at a temperature corresponding to 884.15 K, they are minimal.

Thus, it can be said that hydrogen is desorbed from the getter at 884.15 K, it is the most pure and compared with the hydrogen desorbed from getter at all temperatures less than this.
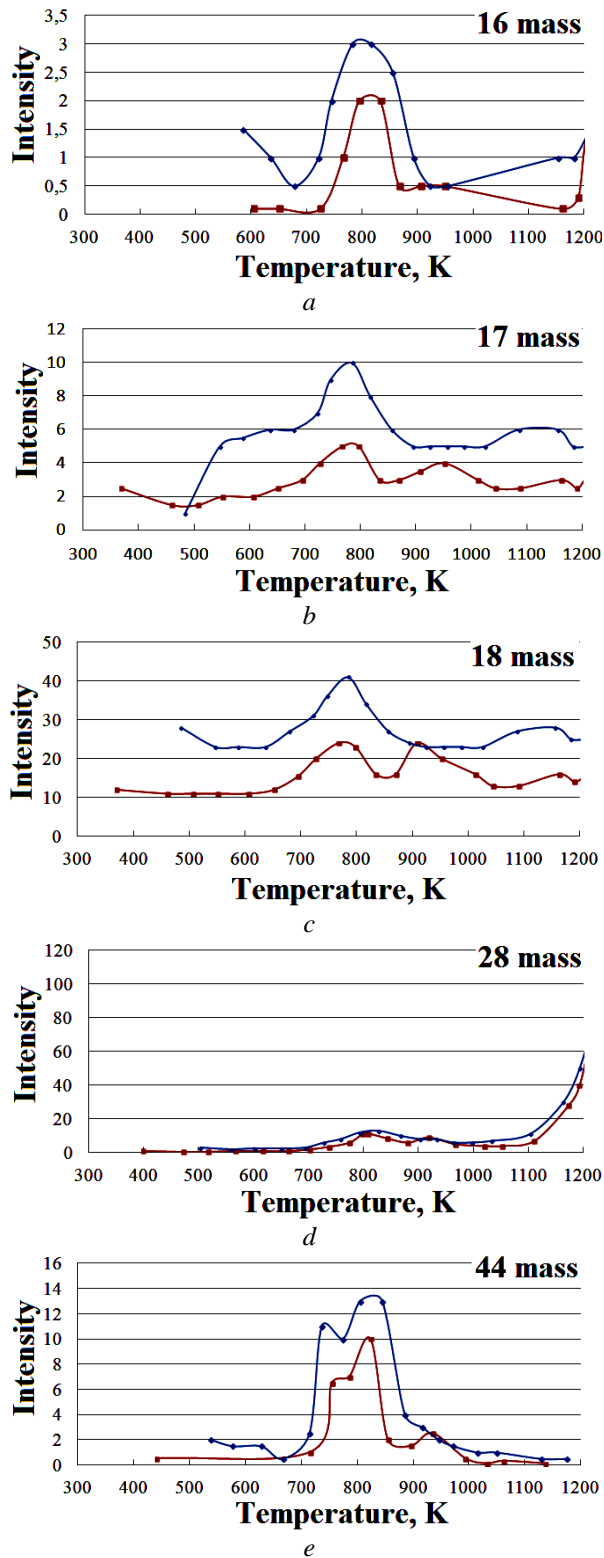

Fig. 2. Partial pressure dependences of gases with mass numbers from 16 to 44 that released from samples:

■ – before thermal treatment;
♦ – after thermal treatment

The hydrogen TPD spectrums used to evaluation the E_{act} magnitude in his "traps" on a scale-up on the temperature axis, shown in Fig. 3. They show that the position of the maxima of desorption depends on the sample heating rate and with it an increase in the spectra are shifted to higher temperatures. There are new inflection points, plateaus, and highs on the curves of the spectra.
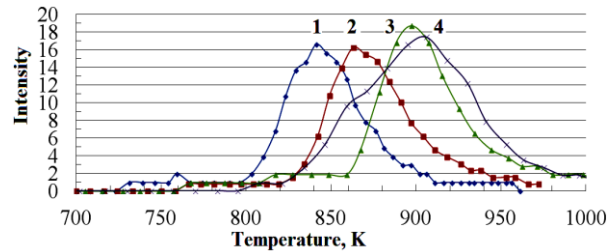

Fig. 3. The hydrogen TPD – spectrums given from Zr (62) – Ni (38 wt.%) getter after heating for several of heating rates:
1 – 13 K/min, T_{max}=841.15 K;
2 – 15 K/min, T_{max}=863.15 K;
3 – 20 K/min, T_{max}=897.15 K;
4 – 25 K/min, T_{max}=906.15 K

The value E_{act} of hydrogen desorption was calculated according to the formula proposed by Redhead [10]:

$$\frac{E}{R \cdot T_{max}} = \frac{\ln(\gamma_1 \cdot T_{max})}{\beta} - 3.64, \qquad (1)$$

wherein E – is activation energy of hydrogen (E_{act}), $\frac{J}{mole}$; R – is absolute gas constant, $\frac{J}{mole \cdot K}$; T_{max} – is the temperature at which the hydrogen desorption rate is a maximum on the TPD – spectrums, K; γ_1 – is the rate constant, taking 10^{13} s^{-1}; β – is the given desorption rate, K·s^{-1}.

Calculated according to the proposed formula was $E_{act} \approx 250$ kJ/mol. And as E_{act} not much different from E_b [13], the calculated value ($E_{act} \approx 250$ kJ/mol) can be referred to E_b. E_b in the literature lead to other units: kcal/mol or eV/at. In these units, E_b is ~ 59.75 kcal/mole and 2.59 eV.

E_b also has been calculated by a different method – form of hydrogen desorption peaks shown in Fig. 3 [11]. To do this, we used the expression:

$$E_b = \chi \cdot R \cdot T_{max}^2 / \delta, \qquad (2)$$

where χ – is the order of reaction 1 or 2; R – is the absolute gas constant, $\frac{J}{mole \cdot K}$; T_{max} – is the temperature at which the hydrogen desorption rate is a maximum on the TPD – spectrums, K; δ – is a desorption peak half-width at half-height, from the high temperatures, K.

To calculate χ was taken equal to 1, because TPD spectra shape of the curves in Fig. 3 are asymmetrical [9, 10].

As a result of the calculations the average value of E_b was obtained for each curve Fig. 3 equal to ≈ 207 kJ/mol (~ 49.52 kcal/mol; 2.145 eV).

Made in this study estimate E_b using the formulas (1) and (2) to hydrogen "traps" which contained in the Zr (62) – Ni (38 wt.%) getter is in good agreement with the value E_b equal to 243 kJ/mol (58.2 kcal/mol, 2.53 eV) to "traps" a zirconium-based alloy [14].

Defect analysis in the zirconium alloys, carried out in [13, 15], considers contained in them "traps" such microstructural defects as – vacancies, impurities, dislocations, their accumulations and all sorts of combinations, micropores, grain boundaries and areas near them ... ie to localized areas on the surface and within the alloy, where the hydrogen atoms have a lower free energy in comparison with their positions in the lattice.

The above-mentioned defects, as well as others, may be present in samples of almost any solids. This will depend on the prehistory of the sample, its chemical and phase composition. Thus, in this study in the Zr (62) – Ni (38 wt. %) samples getter, such defects are in phase grain boundaries (ZrNi, Zr_2Ni), the boundary between these phases, and possibly other defects. In the literature, the hydrogen "traps" associated with such defects, referred to as weak coupling "traps" [13].

Of course, even greater interests are a strong bond "traps" such as macropores and cracks are present on the surface of the getter. As is known, the hydrogen desorption from the strong bond "traps", which are the materials containing zirconium, as is the case in the test getter occurs at temperatures above 1200 K [13].

In this work, gas desorption wasn't studied at temperatures higher than 1200 K, but the analysis of Fig. 1 (curve 2) shows that the a strong bond "traps" with hydrogen present in the test getter – hydrogen desorption at a temperature corresponding to ~ 1200 K doesn't stop or observed his gradual decline, which would have been otherwise.

Without a doubt, and the maximum value of the bond energy in hydrogen "traps", and the temperature at which the last observed gas desorption is of great interest, since they determine the potential use of the getter material.

Nickel, which is part of the test getter material, is not an element, whose radioactivity, arising under the influence of neutrons reaches a safe level for the time planned for use in the next – generation reactors. However, it will be of interest for use in a wide range of materials to which the requirements are not so strict [16].

It should be noted, and it is very important that TPD – method largely displays imperfections microstructure features of the samples. The spectra were obtained with samples with different chemical and phase composition, but differ little imperfection of its microstructure will give similar in view spectra [17].

CONCLUSIONS

1. The results of these studies have shown that selected for that TPD method is highly sensitive and allows obtaining the necessary information about the properties and the behavior of the materials.

2. Defined hydrogen desorption maximums on the TPD – spectrums and highs of all partial pressures of impurity gases in the partial pressure spectrums.

3. Estimated value of the hydrogen bond energy in his "traps" by two independent methods, which amounted to ≈ 250 kJ/mol and ≈ 207 kJ/mol, respectively.

4. Implementation of using the Zr (62) – Ni (38 wt.%) non – evaporable getter requires the development of appropriate methods of doping it in the test and developed materials.

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ИЗУЧЕНИЕ ПРОЦЕССОВ ДЕСОРБЦИИ ИЗ НЕРАСПЫЛЯЕМОГО ГЕТТЕРА Zr (62) – Ni (38 мас.%), ПОЛУЧЕННОГО ПО КАЛЬЦИЕТЕРМИЧЕСКОЙ ТЕХНОЛОГИИ

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Изучены процессы десорбции из нераспыляемого геттера Zr (62) – Ni (38 мас.%), полученного по кальциетермической технологии. Проведено сопоставление спектров термостимулированной десорбции с образцов, имевших разную предысторию. Показано, что она влияет на их вид. Приведены результаты изменений парциальных давлений газов, выделяющихся из него с увеличением температуры. Оценена величина энергии связи водорода в его «ловушках».

ДОСЛІДЖЕННЯ ПРОЦЕСІВ ДЕСОРБЦІЇ З ГЕТЕРА Zr (62) – Ni (38 мас.%), ЩО НЕРОЗПИЛЮЄТЬСЯ, ОТРИМАНОГО ЗА КАЛЬЦІЄТЕРМІЧНОЮ ТЕХНОЛОГІЄЮ

Г.М. Аксьонова, Ю.П. Бобров, М.М. Пилипенко, О.П. Свинаренко

Вивчені процеси десорбції з гетера Zr (62) – Ni (38 мас.%), що нерозпилюється, отриманого за кальцієтермічною технологією. Проведено зіставлення спектрів термостимульованої десорбції із зразків, які мали різну передісторію. Показано, що вона впливає на їх вигляд. Наведені результати зміни парціальних тисків газів, які десорбують з нього із підвищенням температури. Оцінена величина енергії зв'язку водню в його «пастках».