

Theoretical and Experimental Study of Sorption Processes on Non Evaporable Getters St 707

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Abstract

Non evaporable getters (NEG) are sorption materials widely used in vacuum technology to obtain and to maintain UHV conditions. For its optimal utilization it is important to know what types of interactions are dominant during the sorption process. Theoretical study on the sorption process of molecules H_2 , N_2 , Ar and CH_4 on the NEG St 707 surface has been performed. By the method of empirical potentials the total interaction energy was calculated as the sum of dispersion, repulsion, electrostatic and inductive part of the energy. The NEG surface was represented as a cubic MgCu₂ structure. The energetic profile of approaching of gas molecules to the surface model is evaluated. Theoretical values of sorption energies are in good agreement with experimental values obtained by the method of thermal desorption spectroscopy (TDS). Trapping effect of argon during adsorption of other residual gases was also observed. A low sorption probability of methane molecules on the NEG surface was also theoretically explained.

I. INTRODUCTION

Non evaporable getters are widely used to obtain HV or UHV conditions in particle accelerators, plasma machines, evacuated solar collectors and other vacuum systems. St 707 wafer module strip manufactured by SAES Getters S.p.A. is a ternary alloy consisting of [1]: Zr = 70%, V = 24.6% and Fe = 5.4%. The optimum performance of the St 707 getter is obtained after activation at a temperature of 300-500 °C under dynamic vacuum conditions. For its optimal utilization it is important to know what types of interactions during the sorption process are dominant, these ones can be evaluated according to values of sorption energy.

Theoretical studies of the elementary process of interactions between the surface and gaseous molecules are only at the beginning. If during the interaction of two systems the long range forces are dominant, the interaction energy might be calculated according to the method of empirical potentials.

Values of sorption energies obtained by the method of empirical potentials could be compared by experimental values measured by the method of thermal desorption spectroscopy (TDS). TDS provides the easiest way of predicting outgassing effect inside a vacuum chamber. From the Arrhenius' equation which describes the desorption from the surface a simple expression for calculation of sorption energies was derived [2]. Sorption characteristics of H_2 , N_2 , CO_2 , Ar and CH_4 were measured in the temperature range of 20 - 500 °C. During adsorption of CO_2 on St 707 NEG surface a production of methane was observed.

II. THEORETICAL CALCULATIONS OF SORPTION ENERGIES

A. Methods of empirical potentials

The combination of attractive and repulsive terms give the most types of empirical potentials but they are valid only for the unpolar and uncharged systems. To calculate interaction energies between more complicated systems the terms describing the coulombic and inductive part of interaction energy are added. However, this addition "abolishes the equilibrium" of attractive and repulsive terms but in this time only this is the simplest way to calculate the interaction energy between large polar and charged systems.

The total interaction energy between the sorbent and the gaseous molecule can be approximately divided into the individual contributions of dispersion, repulsive, inductive and coulombic forces:

$$E = E_D + E_R + E_I + E_C \quad (1)$$

The contribution of dispersion (attractive) forces is [3]:

$$E_D = - \sum_i \sum_j C_{ij} r_{ij}^6 \quad (2)$$

Where C_{ij} is the Kirkwood-Muller [4,5] constant

$$C_{ij} = - \frac{3mc^2}{8\pi^2\epsilon_0} \frac{\alpha_i\alpha_j}{\chi_i \chi_j} \quad (3)$$

m is the mass of electron, c is the velocity of light, α_i , α_j are the polarizabilities of interacting particles, χ_i , χ_j are their molar diamagnetic susceptibilities, ϵ_0 is the dielectric permittivity of vacuum, r is the distance of the particles i and j .

The repulsion term is expressed [3]

$$E_R = \sum_i \sum_j B_{ij} r_{ij}^{12} \quad (4)$$

B is a constant determined by conditions of minimal energy for nonbounded interactions

$$B_{ij} = \frac{1}{2} r_0^6 C_{ij} \quad (5)$$

r_0 is the equilibrium distance equal to addition of Van der Waals' radii of interacting atoms.

Induction part of interaction energy is approximated [6]

$$E_I = \sum_j \frac{\alpha_j}{2} \epsilon_j^2(r) \quad (6)$$

α_j is the polarizability of a gas molecule and $\epsilon_j(r)$ is the intensity of electrostatic field created by the surface.

The electrostatic (coulombic) part of interaction energy is given by interaction between the charge distribution in the sorbent q_i and the charge distribution q_j of the sorbed molecules [7]

$$E_C = \frac{1}{4\pi\epsilon_0} \sum_i \sum_j \frac{q_i q_j}{r_{ij}} \quad (7)$$

If the sorbed molecule has no permanent dipol moment but has a quadrupol moment, the electrostatic part of interaction is given

$$E_C = \frac{1}{16\pi\epsilon_0} \sum_i \sum_j q_i q_j (3 \cos^2\delta - 1) r_{ij}^3 \quad (8)$$

where angle δ gives the orientation of the molecule quadrupole moment versus the positional vector r_{ij} .

B. Surface Model and Calculations

The structure of Zr-V-Fe alloys was studied by XPS analysis [8]. These structures could have the cubic structure $Zr(V_xFe_{1-x})_2$ of $MgCu_2$ type with lattice parameters $a = b = c = 0.745, 0.734$ or 0.708 nm. There are 8 $MgCu_2$ molecules in the face centered lattice. Mg atoms are uniformly placed in the distance of 0.291 nm, Mg - Cu distance is 0.305 nm. The surface of St 707 NEG was represented by the known surface of $MgCu_2$, Mg atoms were replaced by Zr atoms and Cu was substituted by V.

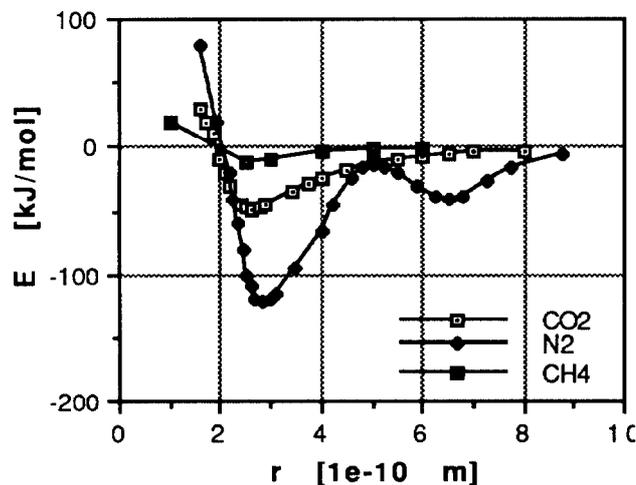


Figure 1. Total energy curves of interactions between the NEG surface and CO_2 , N_2 and CH_4 molecules.

Computer program ADNEG gives a series of curves for dispersion and repulsion part of the interaction energy. Induction and coulombic parts were not evaluated yet, there are no data about the NEG charge distribution published in the literature. Values of atomic polarizabilities, molar diamagnetic susceptibilities and van der Waals' radii of interacting atoms were taken from ref. [9].

There are shown in fig. 1 the curves of total interaction energy with NEG surface for gases CO_2 , N_2 and CH_4 . The value of sorption energy corresponds to the total energy in the deepest minimum of the sorption path.

III. EXPERIMENTAL INVESTIGATIONS OF SORPTION ON THE NEG SURFACE

A. Experimental Apparatus and Procedure

A WP 950 module with the St 707 NEG alloy was installed in the rectangular stainless steel vacuum chamber. Total pressure changes were measured by cold cathode TPG 300 Penning gauges.

A quadrupole mass analyzer Balzers 420 was used to monitor the thermal desorption of gases, as well as the composition of residual gases in the UHV system. The mass spectrometer was connected to an IBM PS/2 computer through its RS232 interface. Mass selection and scanning was then performed from the computer. During the thermal desorption experiment several masses were selected and their signal intensities as a function of temperature were stored in the computer.

The vacuum system was baked-out at 350 °C for 24 hours while the NEG module was passively activated at 260 °C. The pressure equilibrium after cooling was reached in the range of $e-9$ mbar. Then the NEG module was resistively heated up to 500 °C and the desorption and mass spectra were measured.

After obtaining well reproducible results, the NEG was exposed to the desired amount of test gases at room temperature. When the pressure in the chamber was lower than $5.e-10$ mbar, the NEG was heated up to 500 °C at a constant heating rate. Selected masses and pressure changes were simultaneously monitored.

The sorption energy was evaluated according to expression [2]

$$E = RT_m \left\{ \ln \frac{vT_m}{a} + \ln \frac{1}{\ln \frac{vT_m}{a}} \right\} \quad (9)$$

where R is the gas constant, $v = kT/h$ is a rate constant; k, h are the Boltzmann's and Planck's constants, respectively.

B. Results and Discussions

A typical desorption spectrum is shown in fig. 2, together with the curve of the temperature increase.

This desorption spectrum comprises two peaks: the first at the temperature of 78 °C (351 K), the second at 348 °C (621 K). The analysis of residual gases gives the highest intensity for masses 2 (H_2^+), 16 (CH_4^+ , NH_2^+ , O^+), 20 (Ar^{++} , HF^+), 28 (CO^+ , N_2^+), 40 (Ar^+) and 44 (CO_2^+).

Sorption energies calculated according to expression (9) for both peaks are 96 kJ/mol and 176 kJ/mol, respectively. The lower energy corresponds to the weakly sorbed molecules or atoms which are desorbed from the polymolecular layers.

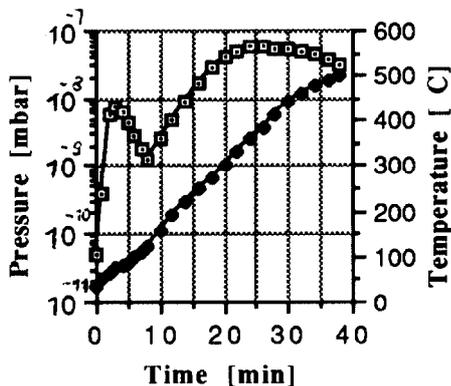


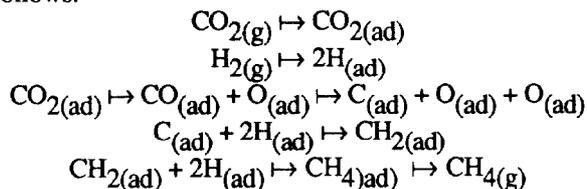
Figure 2. Thermal desorption spectrum and temperature increase.

Desorption and mass spectra after NEG exposure to H₂ did not show significant changes. The first peak was only slightly higher than one on the background TDS spectrum, while the second peak, monitored for mass 2 was always over the measured range of QMA (>e-5 A) because of a large amount of desorbed hydrogen. It can be concluded that only a small amount of hydrogen is physisorbed and a major part diffuses into the bulk of the getter where is chemisorbed.

After NEG exposure to nitrogen the second TDS peak was unchanged, masses 14 and 28 corresponded to the first TDS peak and were much higher than the ones in the background spectrum. Therefore it could be deduced that nitrogen is mostly weakly sorbed with the energy of ~91 kJ/mol.

After NEG exposure to CO₂ the first desorption peak together with masses 44 (CO₂⁺), 28 (CO⁺) and 22 (CO₂⁺⁺) were somewhat higher than those in background spectra, but masses 44 and 22 significantly increased also at the temperature of 250 °C. It could be supposed that CO₂ desorbs through two different desorption features, corresponding sorption energies are 93 and 146 kJ/mol.

During injection of CO₂ into the vacuum chamber the increase of masses 13 (CH⁺), 15 (CH₃⁺) and 16 (CH₄⁺) was observed, which corresponds to methane ion fragments. A plausible scheme of methane production may be formulated as follows:



A dependence of methane production on NEG's temperature surface was also studied. The NEG module at temperatures of 50, 100, 150, 200 and 250 °C was exposed to the same amount of CO₂. No significant influence of NEG temperature on methane production was observed - see fig. 3.

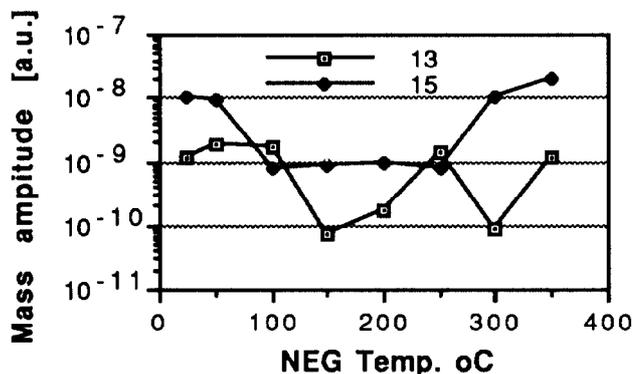


Figure 3. Quantity of CH₄ produced at different NEG temperature.

It is well known that the NEG does not affect noble gases. But in all measured desorption and mass spectra an increase of masses 20 and 40 has been observed. After the NEG exposure to Ar at the temperature of 200 °C and consequent cooling down to 20 °C, the decrease of masses 20 and 40 was also significant. After flashing the NEG to 500 °C also masses 20 and 40 were comprised in the first peak of TDS spectrum.

IV. CONCLUSIONS

A desorption process from the St 707 NEG alloy passes in two steps. In the first desorption peak all masses of residual gas mixture are observed and the trapping effect of Ar could occurred. Theoretical values, in spite of rough approximations, are in quite good agreement with experimental ones. The low sorption probability of methane was confirmed by the shallow minimum on the curve of total interaction energy.

V. REFERENCES

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