New method to determine gas content in materials

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Abstract. A new method to determine gas content in solid materials based on the phenomenon of gas desorption induced by mechanical action, i.e. friction, indentation, etc., has been developed. Absorbed gases including hydrogen and helium can be analyzed using this method in both bulk or thin film materials. The sensitivity of the method for most gases is below 10 ppm of atomic concentration, while depth resolution is below 1 micrometer. The study of the effect of adsorption and readsoption of the desorbed molecules on the accuracy, sensitivity and the dynamic range of measurements is discussed. Experimental validation of the method has been done using normal and deuterated stainless steel samples.

1. Introduction

Mechanical, chemical, optical, electrical and other properties of a large variety of engineering and functional materials can be significantly altered by the presence of hydrogen and other gases in the material bulk and on the surface. Nowadays there are several methods to characterize the gas content in materials and in surface coatings, which can be classified in the following groups: (i) thermal desorption spectroscopy and evolved gas analysis, (ii) vibrational spectroscopies (NMR, UPS, FTIR, GDOS, etc.), (iii) inelastic scattering and energy loss spectroscopies (INS, EELS), (iv) ion beam based techniques (SIMS, ERDA, RBS), (v) nuclear reaction analysis (NRA). Some of these techniques demand large and complex equipment (groups ii-v) while other are destructive and time consuming. Therefore there is a strong demand of a simple method for analysis of the gas content with features of depth profiling and spatial distribution analysis in various fields of modern industry including chemical, mechanical, power engineering, transport, aerospatial sector and other.

A new method is presented based on the phenomenon of tribostimulated desorption in ultra high vacuum [1]. In this method desorption of gases from the material bulk is stimulated by mechanical action, i.e. friction, indentation, rolling, etc., in a special ultra high vacuum system, while the desorbed gases are measured using vacuum gauges and mass-spectrometers. In the present work the theoretical background and limitations of the sensitivity and accuracy of this new method are discussed.

2. Theoretical background

In a first approach the tribodesorption rate $Q_{td}$ can be determined as a sum of two components: $Q^T_{td}$ desorption rate due to total heating of material in and around the contact zone; $Q^S_{td}$ desorption due to
structural modification, e.g. plastic deformation, fracture, etc. For mild friction conditions, i.e. low speed, low normal load and large period of time between consecutive friction cycles on the same surface area, total heating can be neglected, and then the tribodesorption rate can be expressed:

$$Q_{sd} = \frac{dN_{sd}}{dt}$$  \hspace{1cm} (1)

where \(dN_{sd}\) is the number of desorbed molecules during the period of time \(dt\).

For ductile materials tribodesorption is related mainly with plastic deformation [2], thus the number of desorbed molecules can be expressed as function of the volume of plastically deformed material \(dV_w\):

$$Q_{sd} = \frac{dN_{sd}}{dV_w} dV_w$$  \hspace{1cm} (2)

where the first ratio depends on the initial gas concentration in material \(C\) and probability of tribodesorption \(k_{td}^d\):

$$\frac{dN_{sd}}{dV_w} = Ck_{td}^d.$$  \hspace{1cm} (3)

\(k_{td}^d\) is a material characteristic which depends on mechanical, physical and chemical properties of material and temperature. The second ratio in (2) is the rate of deformation of material, which depends on the friction conditions and generally doesn’t depend on the material’s properties.

For brittle materials tribodesorption is related with fracture and craze formation [3], thus the number of desorbed molecules can be expressed as a function of the area of fractured surfaces \(dA_f\):

$$Q_{sd} = \frac{dN_{sd}}{dA_f} dA_f$$  \hspace{1cm} (4)

Assuming that gases are desorbed from the layer of thickness \(h\) with desorption probability \(k_{td}^b\) the first ratio in (4) can be transformed:

$$\frac{dN_{sd}}{dA_f} = Ck_{td}^b h$$  \hspace{1cm} (5)

Finally, the total tribodesorption rate can be determined as a sum of the ductile and brittle components:

$$Q_{sd} = C \left( k_{td}^d \frac{dV_w}{dt} + k_{td}^b h \frac{dA_f}{dt} \right).$$  \hspace{1cm} (6)

The total number of desorbed gas molecules is determined by integration of (6) in the time interval from \(t_0\) to \(t_f\), which are the time of the beginning and termination of tribodesorption, correspondingly:

$$N_{sd}^S = \int_{t_0}^{t_f} C \left( k_{td}^d \frac{dV_w}{dt} + k_{td}^b h \frac{dA_f}{dt} \right) dt = C \int_{0}^{V_w} k_{td}^d dV_w + C \int_{0}^{A_f} k_{td}^b h dA_f.$$  \hspace{1cm} (7)

If the tribodesorption probabilities are constant in time, the eq. (7) can be further simplified:

$$N_{sd}^S = C(k_{td}^d V_w + k_{td}^b h A_f),$$  \hspace{1cm} (8)

where \(V_w\) and \(A_f\) are the total deformed volume and the total fractured area during the time interval \([t_0,t_f]\). So, the initial concentration of gas in the material can be found as following:

$$C = \frac{N_{sd}^S}{k_{td}^d V_w + k_{td}^b h A_f},$$  \hspace{1cm} (9)
where \(N_{id}^S\), \(V_w\) and \(A_f\) are determined experimentally, while \(k_{id}^d\) and \(hk_{id}^b\) should be determined by calibration using standard samples.

3. Experimental

The developed model was applied to the experimental data and the unknown desorption probability was determined. Tribodesorption was measured during reciprocating friction of AISI 304 stainless steel samples in high vacuum using an alumina ball of 3 mm diameter with normal load 216 mN, sliding velocity 38 cm.s\(^{-1}\) and sliding frequency 2 cycles per second \([4]\). Total pressure and partial pressures of various gases were measured simultaneously during friction using ionization gauge and a quadrupole mass-spectrometer, correspondingly. After finishing the experiment the sample was taken of the system and the cross-section profiles of wear scars were measured using stylus profilometer.

The total number of desorbed molecules \(N_d\) was calculated by integration of the \(p-t\) curves as described in \([5]\). The first portion of the graph \(N_d\) vs. time is shown in Fig.1. The calculation gives \(7.5 \times 10^{14}\) desorbed molecules after 1000 friction cycles, while the volume of the wear track was \(1.74 \times 10^{-7}\) cm\(^3\). The volume of the wear track was calculated as a product of the cross-section area of the wear track (Fig. 2) and its length \(l=7\) mm. No brittle fracture was observed, so the second term in the denominator in (9) is nil. The initial concentration of hydrogen in this material was \((3.4\pm1.8) \times 10^{19}\) at.cm\(^{-3}\). Thus, it was determined from (9) \(k_{id}^b = 254\) with the dispersion interval (166; 539). Such high value of \(k_{id}^b\) indicates that much larger volume of material \(A_d\) than considered is involved into tribodesorption (Fig. 2). These conclusions are consistent with early works of Kragelsky et al. \([1]\), who first proposed to distinguish active volume for desorption and worn volume.

![Figure 1](image1.png)

**Figure 1.** Number of desorbed molecules vs. time during first 200 friction cycles.

![Figure 2](image2.png)

**Figure 2.** Cross-section of the wear track. \(A_w\) is the cross-section area of the wear track. \(A_d\) is the zone contributing to tribodesorption.

The developed method can be used also for analysis of the isotopic composition of the dissolved gases \([5]\). This method was used to determine the relative deuterium concentration in absorbed hydrogen in stainless steel previously doped with deuterium using electrolytic method. Tribodesorption rate of H\(_2\), HD and D\(_2\) was measured and then the D/H ratio was calculated. In these experiments the relative D/H concentration as small as \(1.8 \times 10^{-3}\) was measured.

4. Assessment of sensitivity and accuracy of the method

Sensitivity of the method is limited by the minimal number of desorbed molecules, which can be measured by the given method. The measuring limit of the number of desorbed molecules is a function of the gas species and depends on the composition of the residual vacuum. For gases, which are not present in the residual vacuum, e.g. Ar, the measuring limit for the desorption rate can be as low as \(10^9\) mol.s\(^{-1}\), while for the gases like H\(_2\), CO, CH\(_4\) and other the measuring limit depends on their partial pressures. By increasing \(V_w\) very high sensitivity can be obtained, however, as \(V_w\) increases the spatial
resolution of the analysis decreases. For the spatial resolution of 1 mm the sensitivity of the method for hydrogen in stainless steel is estimated below 0.4 ppm (wt.).

Using of vacuum system for measuring the number of desorbed molecules introduces a systematic error related with readsorption of the molecules on the surfaces of the vacuum system and on the sample. A model of readsorption was developed on the basis of the equations of mass balance in the adsorbed phase and in the gas phase. The number of readsorbed molecules was calculated for a vacuum system used in our experiments, which has the following characteristics: volume 14 l, internal surface area 0.38 m², pumping speed for H₂ at 295 °C is 27.7 l.s⁻¹. Figure 3 shows the ratio of the calculated number of readsorbed molecules to the experimentally measured number of desorbed molecules.

![Figure 3](image)

For the studied pressure range \( N_{a,\text{vs}} \) does not exceed 10% of the number of desorbed molecules in UHV and it is below 1% for pressures higher than \( 10^{-7} \) Pa. Thus, readsorption of molecules on the walls has small or insignificant effect on the accuracy of tribodesorption measurements.

5. Conclusions

A phenomenological model for tribodesorption showed that the tribodesorption rate and the total number of desorbed molecules are proportional to the initial concentration of gas in the bulk material and inversely proportional to the mechanically affected volume of material. The proportionality constant is a material characteristic, which can be determined by calibration using standard samples.

The sensitivity of the method depends on the type of the gas and it is inversely proportional to the volume of mechanically affected material. For the volume of the order of several cubic millimetres the sensitivity for hydrogen can be as low as 0.4 ppm (wt.). Readsorption of molecules on the walls has small or insignificant effect on the accuracy of tribodesorption measurements.

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References

[1] Roman E, Nevshupa R A, de Segovia J L, Menshikov I P and Konovalov P I Method and apparatus for analysis of gas content in solids and surface coatings. Patent application No. ES200700480 on 23/02/2007.
[2] Kragelski I V, Lubarski I M, Gusliakov A A et al. Friction and Wear in Vacuum, Mashinostroenie, Moscow, 1973. (in Russian)
[3] Dickinson J T, Jensen L C, Langford S C and Hirth J P, 1991 J. Mat. Res. 6 112.
[4] Nevshupa R A, de Segovia J L and Deulin E A, 1999 Vacuum 53 295-298.
[5] Nevshupa R A, de Segovia J L and Roman E, 2005 Vacuum 80 241-246.