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SYNCHROTRON RADIATION INDUCED NEUTRAL GAS DESORPTION FROM SAMPLES
OF VACUUM CHAMBERS

by

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Abstract:

Synchrotron radiation induced neutral gas desorption from samples of different vacuum chamber materials has been measured at the DCI storage ring at LURE, Orsay. In order to study the effect of a surface oxide layer on the desorption rate and its decrease during continued photon exposure (frequently called beam cleaning), a comparison has been made between lightly and heavily oxidized samples of aluminium and steel (Nimonic). The dependence of the desorption rate for hydrogen on the photon dose and on time for the different types of samples supports a model of gas diffusion from near surface layers and from the bulk to the surface. The experimental set-up also permitted the measurement of the photoelectron current from the different samples and hence comparison with electron stimulated neutral gas desorption measurements in the laboratory on indentially prepared samples.

1. Introduction

In this paper we present the results of measurement of the neutral gas desorption from flat samples of vacuum chamber materials stimulated by synchrotron radiation photons and by electrons. The purpose of this study has been twofold :

1. to evaluate the effect of the omnipresent oxide layer of the surface of the samples of vacuum chamber materials on the neutral gas desorption yield.
2. to compare the molecular desorption yield stimulated by photons (PSD) and by electrons (ESD) on indentially prepared samples.

2. Sample preparation

Two different alloys, aluminium type ISO AlMgSi and a high temperature steel type 'Nimonic' have been selected for our studies, see table 1. From these two materials reference samples have been prepared by a chemical cleaning process consisting of etching in NaOH followed by immersion in HNO₃ and rinsing in demineralized water. As seen by Auger analysis, the surface of these two samples is

characterized by an approximately 40 Å thick oxide layer formed during exposure to air at room temperature. Since one of the main interests has been to investigate the influence of the surface oxide layer on these materials, the aluminium alloy samples have been complemented by a sample of bulk alumina. This specimen has been cleaned by heating at 950°C in air. The high temperature steel sample was complemented by a specimen of the same material which, however, has been subjected to a special high temperature oxidation procedure [1] at 950°C. As a result of this processing a pure and dense 2 µm thick oxide scale of Cr₂O₃ has been formed on the surface. The further common treatment for both, the Al₂O₃ and the oxidized Nimonic samples, has been a heat treatment at 500°C in a vacuum of 10⁻⁸ mbar for 24h.

Unfortunately the Nimonic samples, destined for electron stimulated desorption measurements, were contaminated by an approximately 20 Å thick MgO layer after cleaning.

After their installation in the test system and preceding any desorption measurements, all samples have been baked in situ at 150°C for 24 h.

Table 1: Preparation of all samples

	material	cleaning	heat treatment	bake out in situ
sample 1	AlMgSi	chemical cleaning		150°C
sample 2	Al ₂ O ₃	950°C in air	500°C in vacuum	150°C
sample 3	Nimonic	chemical cleaning		150°C
sample 4	Nimonic oxidized	950°C in H ₂ /H ₂ O	500°C in vacuum	150°C

3. *Molecular desorption yield of photons and electrons*

Experimental set up

The synchrotron radiation induced desorption yield has been measured at the DCI machine at the LURE laboratory Orsay, Paris. The experimental set-up has been described in detail elsewhere [2]. For this experiment, the individual specimens (4.7 by 6 cm) were screwed on a copper plate and mounted on a common sample holder. This support could be rotated to bring the desired specimen in the position where it was exposed to a collimated photon beam of known energy spectrum and intensity at normal photon incidence. The critical energy ϵ_c of the photon spectrum was $\epsilon_c = 773$ eV. The desorbed gas flow and thus the neutral gas desorption yield could be measured with a calibrated residual gas analyser and a set of calibrated total pressure gauges and a known pumping speed.

The sample holder could be biased with respect to the surrounding vacuum system and thus the photoelectron current from each sample under the conditions of the experiment could be measured. This method failed, however, to give meaningful results in the case of the alumina (sample 2) and oxidized Nimonic (sample 4) samples because of their insulating properties.

The data for electron stimulated desorption have been obtained by laboratory measurements [3] in a vacuum system similar to the photon desorption set-up. Here, the samples were exposed to electrons emitted from a hot filament and accelerated towards the positively biased sample holder. The bombarding electron energy was chosen to be 300 eV. Because of the insulating properties of the Al_2O_3 sample it was not possible to obtain reliable results for the electron stimulated desorption.

Measurement

The molecular desorption yield for the main desorbed gases $\text{H}_2, \text{CH}_4, \text{CO}, \text{CO}_2$ has been derived from the flux of desorbed gas Φ , under either photon or electron bombardment. The initial desorption yields η at the first exposure of a sample are summarized in Table 2. Also included is the measured photoelectron yield ρ . The ESD results of the Nimonic samples might be influenced by the contamination with the surface MgO layer.

During the photo desorption measurements special attention has been given to reduce the 'dynamic background' caused by desorption from the surrounding test chamber due to scattered photons and secondary electrons. Therefore, to account for this effect the contribution of the dynamic background to the total flow of desorbed molecules has been estimated by exposing a dummy sample to a high dose of bombarding photons. In the case of closed geometries like vacuum chambers the secondary electrons and scattered photons can cause an increased secondary desorption.

Table 2: Initial desorption yield η

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		PSD	PSD	PSD	PSD	ESD	ESD	ESD
sample		AlMgSi 1	Al ₂ O ₃ 2	Nimonic 3	Ni. - Oxide 4	AlMgSi 1	Nimonic 3	Ni - Oxide 4
H ₂	η	1.9 10 ⁻³	2.0 10 ⁻³	1.2 10 ⁻³	1.1 10 ⁻³	1.0 10 ⁻¹	1.1 10 ⁻³	1.0 10 ⁻¹
CH ₄	η	5.7 10 ⁻⁴	4.0 10 ⁻⁴	2.2 10 ⁻⁴	2.0 10 ⁻⁴	4.0 10 ⁻³	2.0 10 ⁻⁴	4.0 10 ⁻³
CO	η	1.2 10 ⁻³	1.2 10 ⁻³	4.3 10 ⁻⁴	3.6 10 ⁻⁴	8.0 10 ⁻²	3.6 10 ⁻⁴	8.0 10 ⁻²
CO ₂	η	2.7 10 ⁻³	3.4 10 ⁻³	1.7 10 ⁻³	1.2 10 ⁻³	1.2 10 ⁻¹	1.2 10 ⁻³	1.2 10 ⁻¹
	ρ	5.5 10 ⁻²		2.8 10 ⁻²				
η		[mol/photon] or [mol/electron]						
ρ		[photoelectrons/photon]						

4. Variation of the hydrogen desorption flux

During continued exposure to photons (or electrons), the initially large desorption yield gradually decreases by the so called process of 'beam cleaning' as observed with synchrotron radiation in electron - positron storage rings. In this paper, we have studied in more detail the evolution of the hydrogen desorption rate.

Model of hydrogen diffusion

To describe the observed dependence of the hydrogen desorption rate on the exposure to photons and to electrons we have assumed that the desorbing hydrogen is first transported by a diffusion process to the surface. Neglecting chemical reactions on the surface, a simplification which appears to be justified in the case of hydrogen, the gas–solid interaction may be characterized by both volume (diffusion) and surface (adsorption, desorption) processes [4,8]. In a simplified, one dimensional model of diffusion, the transport of molecules inside the bulk may be described by

$$\begin{aligned} \partial c / \partial t &= - D \partial^2 c / \partial x^2 & (1) \quad & \text{Transport of the gas molecule via} \\ & & & \text{diffusion inside the solid} \\ \Phi &= K c & (2) \quad & \text{ESD, PSD from the surface region} \end{aligned}$$

where c [$\text{cm}^3(\text{STP}) / \text{cm}^3$] is the gas concentration inside the solid. Because of the long term heat and vacuum treatment c is assumed to be in balance with the surface region. K [cm / s] is a phenomenological constant depending on irradiation current, photon energy spectrum and cross section for desorption. D [cm^2 / s] is the diffusion coefficient in the solid and Φ [$\text{cm}^3(\text{STP}) / \text{s} / \text{cm}^2$] is the desorbed gas flux. In the following the reabsorption is neglected because of high pumping speed and low absorption coefficient for hydrogen in aluminium. So, the net gas flux Φ leaving the surface is given by

$$\Phi = D \partial c / \partial x \Big|_{x=0} = K c \Big|_{x=0} \quad (3)$$

An analytical solutions of eq. (1) with the boundary condition (3) and with a uniform concentration c_0 inside the bulk as a starting condition for a semi–infinite plate is [4,5]

$$\Phi = \Phi_0(t=0) [\exp((K^2 / D) t)] [1 - \text{erf}(\{(K^2 / D) t\}^{-1/2})] \quad (4)$$

From this solution, shown in fig. 1 as a full line, it follows that Φ decreases after an initial time t_0 according to

$$\Phi \propto t^{-1/2} \quad (5)$$

In order to apply this model to measured data the normalized desorption flux Φ/Φ_0 has been expressed as a function of the normalized time τ ($\tau = (K^2/D) t$). This normalisation accounts for periods without radiation as well as for periods with different radiation intensities.

This one dimensional diffusion model has been shown to describe several effects observed during photon bombardment experiments, e.g. non-linearity with radiation intensity, recontamination during an interruption of the photon exposure 'beam stop' [6].

5. Results

1. The diffusion model has been applied to the desorption yield data for hydrogen given in table 2. For this purpose, all measurements have been normalized to Φ/Φ_0 . An initial hydrogen concentration c_0 , ranging between 1.1 and $2.1 \cdot 10^3 \text{ cm}^3(\text{STP})/\text{cm}^3$ has been assumed. The recombination constant K follows in turn from the initial desorption flux according to eq.3. Finally, the ratio K^2/D and hence the diffusion coefficient D , has been obtained by fitting the experimental results of the photon, and the electron dose dependence of the desorption yield. The result of this procedure which reproduces the experimental data very closely is shown in figure 1. It should be noted that for reasons of presentation, the curve for the ESD measurements in this figure has been displaced downwards by one decade.

Tab. 3 gives a summary of the two parameters D and c_0 for all specimens which follow from this analysis. Good agreement between samples (samples 1 and 2 and samples 3 and 4, respectively) with a similar surface oxide is shown as well as between PSD and ESD measurements considering the slightly different temperature. For the Nimonic samples the discrepancy between PSD and ESD measurements is attributed to the MgO layer on the Nimonic samples used for the ESD measurement.

In the case of the aluminium samples, the initial hydrogen concentration corresponds approximately to the hydrogen concentration in aluminium trihydroxide $\text{Al}(\text{OH})_3$ e.g. 'Gibbsite' which is a common product of the room temperature oxidation of aluminium.

Furthermore, the fact that the desorption of the gases H_2 , CH_4 , CO and CO_2 from samples with similar surface oxide ($AlMgSi$ and Al_2O_3 and Nimonic and the oxidized Nimonic) yields similar values of the initial desorption, see table 2, suggests that the gas which is desorbed during photon exposure has its origin in the surface oxide layer.

Table 3: Parameters characterizing the hydrogen diffusion

Photon stimulated desorption		D [cm ² /s]	c ₀ [cm ³ (STP)/cm ³]	T = 20°C
sample 1	AlMgSi	1.5 10 ⁻¹⁸	1.1 10 ³	
sample 2	Al ₂ O ₃	8.7 10 ⁻¹⁹	1.1 10 ³	
sample 3	Nimonic	2.5 10 ⁻¹⁹	1.1 10 ³	
sample 4	Nimonic oxidized	4.0 10 ⁻¹⁹	1.1 10 ³	
Electron stimulated desorption				T ≈ 35°C
sample 1	AlMgSi	6.3 10 ⁻¹⁸	1.1 10 ³	
sample 2	Al ₂ O ₃	— —	— —	
sample 3	Nimonic*	7.0 10 ⁻¹⁸	1.1 10 ³	
sample 4	Nimonic oxidized*	4.6 10 ⁻¹⁸	2.1 10 ³	

* These samples had a (about 20 Å) MgO layer on the surface.

2. The analysis of the desorption yield values for the different specimens has been made with the aim of establishing a comparison between PSD and ESD measurements. In view of the different primary incident particles, a direct comparison of the desorption yield expressed as molecules per photon and as molecules per electron cannot be made. However, it has been found that satisfactory agreement may be obtained if the data are expressed in terms of the desorbed molecules per photoelectron for PSD and converted to desorbed molecules per secondary electron for ESD. A comparison between column 3 and column 5 in table 4 shows that with the exception of CH₄ good correspondence is found. To convert to secondary electrons, the secondary electron coefficient for the AlMgSi sample has been taken from measurements reported in ref. 7. Unfortunately, the corresponding value for the Nimonic sample has not been available.

Table 4: Initial desorption yield η of AlMgSi

	PSD		ESD	
	η	η^*	η	η^*
H ₂	1.9 10 ⁻³	3.5 10 ⁻²	1.0 10 ⁻¹	3.6 10 ⁻²
CH ₄	5.7 10 ⁻⁴	1.0 10 ⁻²	4.0 10 ⁻³	1.4 10 ⁻³
CO	1.2 10 ⁻³	2.2 10 ⁻²	8.0 10 ⁻²	2.8 10 ⁻²
CO ₂	2.7 10 ⁻³	4.9 10 ⁻²	1.2 10 ⁻¹	4.3 10 ⁻²
	ρ	5.5 10 ⁻²	2.8	ref [7]
η	[mol/photon,electron]			
ρ	[photo or secondary electron/photon or electron]			
$\eta^* = \eta/\rho$	[mol/secondary electron]			

6. Summary

The analysis of electron and photon stimulated neutral gas desorption experiments indicates that the following processes effect the desorption :

- The oxide layer on the examined metals, which seems to be a hydroxide, determines the photon and electron stimulated gas desorption from samples.
- There is some evidence that it is the photoelectrons which are produced by the incident photons, rather than the photons themselves, which dominate the neutral gas desorption from samples. Good correspondence between PSD and ESD measurements are found by expressing the molecular desorption yield in terms of molecules per photoelectron or secondary electron rather than in terms of primary photons and primary electrons.
- The variation of the hydrogen desorption yield with time and with photon or electron dose is determined both by the desorption efficiency of the bombarding photons or electrons and by a diffusion process in the near surface layers.

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