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Prepared for Presentation
2nd International Conference
On Surface Effects in Controlled Fusion Devices
San Francisco, Ca.
February 16-20, 1976

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X-Ray Impact Induced Desorption of Gases from Surfaces[†]

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Abstract

Measurements of gases released from 302 stainless steel and gold surfaces before and after discharge cleaning were made in ultrahigh vacuum using x-rays with an energy distribution typical of a tungsten bremsstrahlung spectrum. Similar measurements were also made for Al_2O_3 surfaces which had not been discharge cleaned. For the non-discharge-cleaned surfaces of stainless steel, Al_2O_3 , and gold the predominant gas species observed mass spectrometrically was CO_2 . For some stainless steel and Al_2O_3 surfaces CO and O_2 were also readily observed. Mean quantum yields for CO, O_2 and CO_2 release from such stainless steel surfaces, for example, ranged from $< 6 \times 10^{-5}$ to 9×10^{-4} molecules per photons in the bremsstrahlung spectrum characteristic for 50 keV electron energy. After discharge cleaning a decrease in the mean quantum yields was observed for the stainless steel and gold surfaces.

Introduction

The irradiation of solid surfaces by energetic photons can lead to the release of gases through such processes as photodesorption, photodecomposition and photocatalysis. Photon induced gas release processes from surfaces is of interest in connection with the controlled thermonuclear fusion research program, since the release of gaseous impurities from irradiated components can lead to plasma contamination. This contamination in turn can lead to an enhanced plasma resistivity and power losses via bremsstrahlung, line, and recombination radiation [1]. In both existing plasma containment devices and proposed fusion reactors the surfaces of major components such as container walls, divertor walls and beam limiters will be exposed to photons with a broad energy spectrum. These photons will appear as γ -rays, x-rays, line and recombination radiation, bremsstrahlung, and synchrotron radiation.

The problem of photon induced degassing as a contribution to vacuum system contamination has been investigated for electron storage rings [2, 3] and for aluminum and stainless steel vacuum chambers exposed to fission reactor irradiation [4, 5]. The release of gases from solid surfaces under low-energy photon impact will be discussed by Lichtman et al. in another paper in these proceedings.

For high-energy photons in the x-ray region the authors are not aware of any studies of gas release from surfaces under ultrahigh vacuum conditions and the use of mass spectrometry for the identification of the species released. Therefore, studies were begun of the type of gas species and the amount of gas released from 302 stainless steel surfaces under ultrahigh vacuum conditions using mass spectrometric detection and photons in the 10 - 50 keV range. Preliminary results obtained for non-discharge-cleaned stainless steel and Al_2O_3

surfaces were reported recently [6, 7]. The present experiments extend these studies to non-discharge-cleaned gold surfaces and to 302 stainless steel and gold surfaces after discharge cleaning. Results for stainless steel surfaces after discharge cleaning at different CO partial pressures in the 10^{-10} to 10^{-8} torr range are included.

Experimental Procedures

The x-rays were produced by a General Electric XRD-6 X-ray generator with a tungsten-target x-ray tube. The electron energy was variable from 15 to 50 keV and the current from 1.5 to 100 mA. The x-ray spectrum was a tungsten bremsstrahlung spectrum filtered by two beryllium windows (one a 0.76 mm thick window of the x-ray tube and one a 0.89 mm thick window of the chamber). Photon flux values were determined from the dose rate per unit area at the target position using an air-filled ionization chamber (Victoreen Model 621). A more detailed description of the apparatus and of the dose rate calibration has been given earlier [6, 7]. In order to determine the photon flux for a given electron energy, the tungsten Bremsstrahlung spectrum [8] for that electron energy was divided into 5 keV energy intervals. The fraction of the photon flux per energy interval was obtained from the dose rate for this energy interval and from the conversion of the dose rate (Roentgen $\text{cm}^{-2} \text{hr}^{-1}$) into a photon flux (number of photons $\text{cm}^{-2} \text{sec}^{-1}$) [6, 7, 9]. In the conversion it was assumed that for each 5 keV energy interval the photons had an average energy equal to the energy at the midpoint of that interval. The photon fluxes determined this way for different energy intervals at various electron energies have been reported earlier [6, 7]. The stainless steel chamber was pumped by a combination of sorption, titanium sublimation, and ion pumps and the normal background pressure during an experiment was 1×10^{-9} torr. The x-ray beam was collimated and a beam stop was used to minimize the irradiation of the chamber surface area by x-rays.

The targets used for irradiation were type 302 stainless steel foils, .01 cm thick, gold foils, 0.025 cm thick, and Coors AD 995 polycrystalline α - Al_2O_3 vaporization substrates, with an area of 6.4 cm^2 and a thickness of 0.76 cm. These Al_2O_3 targets were obtained in two separate shipments from Dr. Frank Clinard, Los Alamos Scientific Laboratory. The irradiated target area had a diameter of 2.2 cm. The reproducibility of the data was checked by using more than two targets of the same material. The preparation of all targets consisted only of a degreasing procedure with successive ultrasonic bath cleanings in trichloroethylene, acetone, and methanol. The targets were kept in the chamber during a 24 hour bakeout at a temperature of 150°C and then were held at 1×10^{-9} torr for at least 24 hours before irradiation.

The chemical composition of the target surfaces prior to irradiation was studied using Auger Electron Spectroscopy (Physical Electronics Auger Electron Spectrometer). Carbon was observed as a major contaminant in the spectra for both the stainless steel and the Al_2O_3 surfaces. For the discharge cleaning an argon discharge (at 100 μm argon partial pressure, 400 volts) was produced between the target and a Ta electrode of 4 cm^2 area. This procedure was followed in both the Auger spectrometer chamber and the irradiation chamber. The discharge cleaning reduced the initial carbon signal intensity for a 302 stainless steel surface by a factor of 25. Since the irradiation experiments were normally started 15 hours after the discharge cleaning at a background pressure of 1×10^{-9} Torr, it was ascertained by Auger analysis that the carbon build-up during this time (targets held in Auger spectrometer chamber at a higher background pressure of 1×10^{-8} Torr) reached only 15% of the initial value. These results obtained in the Auger spectrometer chamber confirm the validity of this cleaning procedure as used

in the irradiation chamber where in situ Auger analysis was not possible.

The use of this cleaning procedure, however, does not imply that the surfaces are free of adsorbed gas species.

Calibration experiments were used to determine the quadrupole mass spectrometer (Extranuclear Laboratories) response to the particle fluxes of such gases as CO, O₂, and CO₂. The flux sensitivity for the mass spectrometer was found to be 1×10^{21} molecules cm⁻² sec⁻¹ amp⁻¹ for CO, 3×10^{21} molecules cm⁻² sec⁻¹ amp⁻¹ for O₂, and 2×10^{21} molecules cm⁻² sec⁻¹ amp⁻¹ for CO₂.

The mass spectrometer signal change for a particular gas species released by x-ray irradiation was determined for two cases: (1) the x-ray beam striking the target and (2) the x-ray beam striking a beam stop 30 cm from the ionizer region of the mass spectrometer (the target had been removed). Such signals were later corrected for the background signal contribution by subtracting the value obtained with no target in position. A rapid rise and fall of the signal was observed as the x-ray beam irradiates the target (x-rays on) and when the irradiation is stopped (x-rays off).

We have made an estimate of the power density deposited in the first 1000 Å of the target thickness by a 15 keV and a 50 keV x-ray beam for the maximum beam intensity used in these experiments, and we find negligibly small values of $\sim 5 \times 10^{-6}$ W cm⁻² and 1×10^{-5} W cm⁻², respectively for stainless steel. The corresponding values for Al₂O₃ are even less. We consider a thickness of 1000 Å to be much larger than the actual thickness which can contribute to the observed gas release. In fact, for the two energies mentioned above the total power density deposited in the entire stainless steel target thickness of 0.01 cm is only 2×10^{-3} W cm⁻² and 6×10^{-3} W cm⁻², respectively. Such small power densities should not raise the target temperature more than 1°C for the heat transfer conditions (good thermal contact with heavy target holders)

applicable to our experiments. The observation of the rapid decrease in the mass spectrometer signals for the gas species released from surfaces after the x-ray beam was turned off is considered experimental evidence that thermal effects can be neglected.

Results and Discussion

For the non-discharge-cleaned stainless steel and Al_2O_3 surfaces, the species which show the greatest increase in signal during x-ray irradiation, relative to their values without irradiation, are $m/e = 32$ (O_2) and $m/e = 44$ (CO_2). For the non-discharge-cleaned gold surfaces $m/e = 44$ (CO_2) showed the greatest relative increase in signal during x-ray irradiation. Only small relative changes (of the order of $\leq 1\%$) in the intensity of the following major mass peaks were observed: 2 (H_2), 16 (O and CH_4), 18 (H_2O), and 28 (CO and N_2). For the discharge-cleaned surfaces of both stainless steel and gold the relative changes in the intensity of all species was of the order of $\leq 1\%$. These results were obtained using a photon flux of 7×10^{12} photons $\text{cm}^{-2} \text{sec}^{-1}$ from a 50 keV electron energy bremsstrahlung spectrum. It is of interest to note that when the stainless steel and Al_2O_3 targets were heated, the dominant species released by thermal desorption were H_2 , H_2O , CO , and CO_2 . Under photon irradiation, however, only small relative increases are observed for the species H_2 , H_2O , and CO , while the largest relative increases were observed for O_2 and CO_2 . The release of CO_2 from surfaces of such materials as stainless steel and ZnO under photon impact has been observed for distinctly different regions of photon energy (energy range 2 - 7 eV, γ -ray range) [5, 10, 11].

From the values of the incident photon flux and the measured photon-induced molecular flux we have attempted to calculate some mean quantum yields for the release of CO , CO_2 , and O_2 for the x-ray photons from a 50 keV tungsten

Bremsstrahlung spectrum. These mean quantum yields for gas release are expressed as the total number of molecules of a particular gas species released per total number of photons in a bremsstrahlung spectrum at 50 keV electron energy (truncated at 10 keV). Such mean yield values are shown in Table 1.

The values listed in Table 1 have been corrected for the background x-ray induced signal change. The last line gives the minimum gas release yield which could have been detected. This value was calculated from the smallest photon-induced signal change which could be distinguished from the photon-induced background signal change. The quoted yield values are estimated to be accurate only within a factor of five, in view of the uncertainties in the determination of both photon and molecular fluxes. The spread in the mean quantum yields for the non-discharge-cleaned targets of the same material, as listed in Table 1, represents the upper and lower limits of such yields obtained from five targets of the same material in independent irradiation runs. One notices in Table 1 that the mean quantum yield values for the O_2 and CO_2 release from a stainless steel surface (target B) after discharge cleaning are lower than the corresponding values for the non-discharge-cleaned surface. For a discharge-cleaned gold surface a decrease in the mean quantum yield could only be determined for the CO_2 release since the yield values for CO and O_2 were at or below the detection limit even for the non-discharge-cleaned surface. The mean quantum yields for CO_2 release from non-discharge-cleaned stainless steel and Al_2O_3 surfaces were reported recently [7] to decrease with increasing mean photon energy. The mean photon energy dependence of the mean quantum yield for gas release was correlated with the photon energy dependence of the photon absorption coefficient of the substrate material [7].

In order to explore the possibility of photon induced CO oxidation as a mechanism for the CO₂ production, the intensity of the photon-induced CO₂ signal was measured for various partial pressures of CO at an initial total operating pressure of $\sim 1 \times 10^{-9}$ Torr. For a discharge-cleaned stainless steel surface (irradiated with photons from a 50 keV bremsstrahlung spectrum, 7×10^{12} photons cm⁻² sec⁻¹) the amount of CO₂ release was found to be independent of the CO partial pressure for the pressure range studied, as illustrated in Figure 1. Similar results were obtained for non-discharge cleaned stainless steel and alumina surfaces, as reported recently [7].

It should be mentioned that an estimate of the CO₂ gas release rates from non-discharge-cleaned stainless steel has been made recently [6] for the relevant UWMAK-I parameters [12] (bremsstrahlung power loading of 28.2 W cm^{-2}) and assuming that the bremsstrahlung spectrum is typical for a tungsten bremsstrahlung spectrum at 30 keV electron energy. A release rate of 1×10^{13} molecules cm⁻² sec⁻¹ was obtained. Such a high value will contribute to the plasma contamination of fusion devices for as long as the photon-surface interactions release CO₂ with the high yields quoted.

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[†]Work performed under the auspices of the Energy Research and Development Administration.

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Figure Caption

Figure 1. Amount of CO_2 released from a discharge-cleaned stainless steel surface under x-ray irradiation as a function of CO partial pressure.

TABLE 1

Mean quantum yields for gas release in molecules released per photons for a
bremsstrahlung spectrum at 50 keV electron energy and 7×10^{12} photons $\text{cm}^{-2} \text{sec}^{-1}$

		CO	O ₂	CO ₂
Without Discharge Cleaning	Stainless Steel Target A	2×10^{-4}	2×10^{-4}	4×10^{-4}
	Stainless Steel Target B	$< 6 \times 10^{-5}$	5×10^{-5}	2×10^{-4}
	Al ₂ O ₃ Target A	1×10^{-4}	1×10^{-4}	2×10^{-3}
	Al ₂ O ₃ Target B	$< 6 \times 10^{-5}$	$< 3 \times 10^{-5}$	8×10^{-5}
	Gold Target A	6×10^{-5}	$< 3 \times 10^{-5}$	1×10^{-4}
After Discharge Cleaning	Stainless Steel Target B	$< 6 \times 10^{-5}$	$< 3 \times 10^{-5}$	6×10^{-5}
	Gold Target A	6×10^{-5}	$< 3 \times 10^{-5}$	3×10^{-5}
	Detection Limit	6×10^{-5}	3×10^{-5}	3×10^{-5}

Figure 1