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CO Adsorption on Al-Zr at Room Temperature[‡]C. H. Wu,^{*} R. L. Moore, and S. A. Cohen

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ABSTRACT

A study of CO adsorption on room temperature Al-Zr has been done using Auger electron spectroscopy and gas pressure measurements. The atomic surface composition of clean Al-Zr surfaces prepared in UHV by Ar⁺ sputtering, was measured as a function of CO pressure and exposure time. The adsorbed C and O have the same rate constants and surface concentrations for exposures less than 2 Langmuir. Above this exposure quasi-saturation occurs. The measured sticking probability of CO on Al-Zr is constant, $S = 0.7 \pm .3$, for fractional coverage $\theta \leq 0.5$. Above this point S decreased rapidly. The effect of surface roughness on the apparent sticking coefficient has been calculated by a Monte-Carlo simulation. Reactivation of Al-Zr by heat treatment to 700°C has also been studied.

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I. Introduction

Gettering materials have found wide use¹ in tokamaks to control the density of hydrogenic plasmas and to remove the chemically active residual impurity gases such as carbon monoxide, oxygen, nitrogen and water vapor. Pumping of hydrogen isotopes proceeds via the reversible processes of adsorption and bulk diffusion. The pumping of oxygen, nitrogen, carbon monoxide, and water is irreversible, though at elevated temperatures diffusion of N, C, and O into the bulk occurs. They combine with the gettering material to form highly stable chemical compounds which are not desorbed. Thus it is possible to control the hydrogen inventory in the getter without adversely affecting plasma purity and to consider using getters in deuterium-tritium fueled tokamaks such as TFTR.²

The two primary candidates for TFTR gettering materials are Al-Zr and titanium. While both have been used widely in ultra-high vacuum systems^{3,4} the gettering properties of titanium⁵ and pure zirconium⁶ and aluminum⁷ have been studied in more detail. The sorption of residual gases affects the getter pumping speed for hydrogen, poisoning, and reactivation properties. As in step in comparing this aspect of the two candidates, we have studied CO adsorption on room temperature Al-Zr as a function of CO pressure and exposure time. The techniques employed were Auger electron spectroscopy, scanning electron microscopy, and gas adsorption rate monitoring. Reactivation of Al-Zr by in-situ heat treatment was also studied.

II. Experimental Procedure

The apparatus used for this study was a PHI scanning Auger electron spectrometer. An ion pumped ultra high vacuum system keeps the residual pressure in the main chamber below 5×10^{-10} Torr. Samples of Al-Zr (40/60

atomic percent) provided by SAES Getters SPA Company were mounted on a heating stage⁸ to allow regeneration at temperatures up to 700°C. A micrograph of the surface is shown in Figure 1. Before each experiment the sample was cleaned by Ar⁺ sputtering until steady state was achieved, wherein the surface had approximately the same atomic composition, determined by AES in the usual manner,⁹ as the bulk. Atomic concentration on the surface were C-3%, O-5%, Zr-63%, and Al-29%. This is not surprising since the escape depth¹⁰ of the Al and Zr Auger electrons are longer than 30 Å. The adsorption studies were carried out in the pressure range of 10⁻⁸ to 10⁻⁶ Torr of CO(g). Pressures of CO were measured by a Bayard-Alpert ion gauge and a quadrupole mass spectrometer, both of which were calibrated against two Baratron micromanometers. Though the quoted accuracy for the Baratrons is better than 1%, we assume an accuracy of only ±25% since our adsorption studies were done in a lower pressure region than the calibration. The CO gas was admitted to the chamber through a sapphire UHV valve. Its purity, as determined by the mass spectrometer, was ≥ 95%. During adsorption experiments the CO introduced was continuously pumped, a constant pressure being maintained by manual control of the flow rates. In these exposures the predominant residual gases were H₂, H₂O and N₂. During pumping speed measurements the ion pump valve was closed, a burst of CO was injected into the chamber, and the pressure changes were monitored. In these exposures the predominant residual gases were H₂ and CH₄. The peak-to-peak heights as well as complete dN/dE Auger spectra for carbon, oxygen, aluminum, and zirconium were monitored during exposure of the sample to CO gas.

A study of reactivation was made by exposing the sample to 1 x 10⁻⁶ Torr of CO for 20 minutes, heating the sample in situ to ~ 700°C and cooling it to room temperature. The sample was then again exposed to 1 x 10⁻⁶ Torr of

CO and the Auger spectra recorded as a function of time.

The primary electron beam energy was 3 keV. The effect of electron bombardment on the adsorbed gas was determined to be negligible by comparing gas coverages monitored continuously versus those monitored at regular intervals.

III. Results

The Auger peak-to-peak (p/p) heights of oxygen (503 eV), carbon (272 eV), zirconium (147 and 1845 eV), and aluminum (1396 eV) were monitored during exposure of the sputter cleaned Al-Zr samples to CO. In section IV we will use these data on C and O uptake to estimate changes in atomic concentrations on the Al-Zr surface and then to calculate the sticking coefficient of CO. Fig. 2 shows the p/p height for oxygen and carbon as a function of exposure time for three different CO pressures. It can be seen that the change in the oxygen signal on the clean Al-Zr surface occurs in three distinct stages. First, for exposures up to 2L, there is a rapid linear increase. This is followed by quasi-saturation. In the third stage, the oxygen signal continues to increase, but at an increasingly slower rate. The rate of increase of the oxygen signal is proportional to the CO pressure. The p/p height of O at quasi-saturation (O_{qs} , defined as the knee in Figure 2) is independent of pressure over the range investigated. If during any portion of the exposure the CO is pumped away, the O p/p height remains constant ($\pm 5\%$) for at least 2000 seconds. For carbon, as for oxygen, three distinct stages are found. Again there is an initial rapid linear increase to quasi-saturation. However in the third stage, the C p/p height signal decreases with increasing CO exposure.

Figure 3 shows the oxygen, carbon, aluminum and zirconium (147 eV) Auger p/p heights for a long duration of CO exposure. About 1000 L are required to reach full saturation. The Zr 147 eV signal is seen to decrease a factor of ~ 2 after 20L. The Zr (1845 eV) signal (not shown) behaved in a fashion similar to the Al (1396 eV) line, i.e., it changed less than 10% throughout the entire 1500 L exposure. The low energy Al peak, 68 eV, decreases by a factor of ≈ 5 . Because of overlap of the Al_2O_3 84 eV line with the Zr spectrum it is difficult to determine its change accurately.

The determination of initial sticking probability of CO on Al-Zr has been done via pumping speed measurement in addition to the uptake method. Clean areas, up to $\sim .3 \text{ cm}^2$, were prepared on the Al-Zr by Ar^+ sputtering. To minimize the pumping effect of sputtered Al-Zr which contaminates the wall of vacuum chamber, CO gas was admitted into the system during the last 20 sec of the 80 sec Ar^+ sputtering period. The Al-Zr sprayed onto the system walls was saturated during this CO exposure while the sample area, continuously monitored, was found to remain clean. After this treatment the valve to the vac-ion pump was closed, the pressure rise due to outgassing of the chamber recorded, and a burst of CO was admitted to the chamber. Following the initial rise, the pressure decayed and thereafter returned to the outgassing rate of rise. From the pressure decay we determine the pumping speed.

IV. Discussion

1. General

The linear rise in the C and O p/p signals for exposures less than 2 L is similar to the behavior noted⁶ for CO adsorption on pure Zr. The usual explanations for this behavior are either a weakly bound precursor state or a mobile adsorbed state. Since heating of Al-Zr does not result in CO

desorption,^{6,11} the first explanation is the preferred one. The precursor is followed by chemisorption. Applying the standard technique to the data analysis shows that the C and O atomic concentrations are equal for exposures less than 2L. This too favors simple rather than dissociative CO adsorption.

For exposures greater than 5L the O signal increases as the C signal decreases. There are several possible explanations for this. Diffusion of O and C into the bulk is known to occur (at elevated temperatures) and differing diffusion rates for O and C could explain the behavior. However, since the surface concentrations of C and O are constant when the CO gas is removed, we discount the influence of diffusion. Another explanation is that the moderate CO coverages, $\theta \gtrsim .5$, adsorption proceeds only by dissociation, with bound oxide resulting and a carbon atom ejected. The observed behavior could also be explained by artifacts in the AES technique due, perhaps, to differing escape depths.

2. Atomic Concentrations

To convert p/p values to atomic concentrations a model of the adsorbed gas configuration must be assumed. This must include effects of energy dependent electron attenuation lengths, depth distribution of the components, and change in Auger electron yield due to chemical effects. Since the Zr 1845 eV and Al 1396 eV p/p values were not appreciably attenuated by exposure to CO, we conclude that multilayer, $\gtrsim 5\text{\AA}$, CO adsorption did not occur. The attenuation of the Zr 145 eV line may be due, in part, to charge transfer⁶ to the adsorbed CO. To avoid this possible confusion we use the Zr 1845 eV transition.

Using the standard method⁹ we find the concentrations for CO at quasi-saturation are approximately $9 \times 10^{14}/\text{cm}^2$. The uncertainties in this procedure

are mostly due to the assumption of a single CO overlayer. But because of the sensitivity of the calculation to this, we estimate the uncertainty to be $\pm 50\%$ to $\pm 20\%$.

3. Sticking Probability

The sticking coefficient, S , of CO on Al-Zr has been determined by two methods. The first method utilizes the coverage calculated by the method just described, and the usual kinetic expression for the flux

$$\sigma = \frac{3.5 \times 10^{22} \text{ pt}}{\sqrt{mT}} \times S$$

where σ is the coverage in molecule/cm², m is the mass in amu, T is the temperature in K, and p is the pressure in Torr. From this a value $S = 0.75$ is found for coverages $\theta < 0.5$ monolayers. Uncertainties arise from the method of determining the atomic concentrations and the partial pressure measurement. The overall error is estimated to be $(\pm 55)\%$. The dependence of S on θ is shown in Figure 4.

The second method for determining S is via the pumping speed measurement described in section III. One obtains an initial sticking probability $S_0 = 0.7 \pm 0.3$. The uncertainty arises from the absolute pressure determination, the area sputtered, and the measure of the pressure decay rate.

A number of studies have been made of the interaction of carbon monoxide with clean refractory transition metal surface. For example, the saturation coverage for carbon monoxide on polycrystalline Re, W, Mo, and Rh at 300 K are available, and the average value is $\sim 1 \times 10^{15}$ molecule/cm. This agrees very well with the recent result of CO on Zr given by J. S. Foord et al. Both these saturation coverages and sticking coefficient are in

reasonable agreement with the values we have found for Al-Zr. In contrast, the sticking coefficient of O_2 and CO on Al is $\approx 1 \times 10^{-2}$.

To study the effect of surface roughness on the apparent sticking probability, a calculation by Monte-Carlo simulation was performed. We assumed that:

- 1) the geometry of the Al-Zr was plane parallel grooves of constant angle;
- 2) S was independent of angle of impact; and
- 3) the incident flux was isotropic.

Defining S_r as real sticking probability, S_m as the measured sticking probability and ϕ as the groove angle, the ratio S_r/S_m as function of ϕ is shown in Fig. 5. From Figure 1, it is estimated that $\phi = 30^\circ$, so that a value of $S_r/S_m = 0.95$ is obtained.

4. Reactivation of Al-Zr Getter by Heat Treatment

B. Ferrario and Rosai⁴ have reported that the Al-Zr getter can be regenerated by heat treatment after the getter has been saturated with hydrogen. The study of the regeneration of CO contaminated Al-Zr getter is important in the removal of active gases in tokamaks. C and O Auger peak-to-peak height have been monitored continuously during the regeneration process. Figure 6 shows the C and O peak-to-peak signals on Al-Zr as functions of time during the course of the experiment. Region A of Figure 6 shows the uptake of CO upon exposure to 1×10^{-6} Torr of CO at room temperature. Region B shows the rapid decrease upon heating to a final temperature of $\approx 700^\circ\text{C}$ at a background pressure of $\leq 10^{-9}$ Torr. As the sample cools (Region C) to room temperature the CO concentration slowly increases, probably due to residual gas contamination. Reexposure to 10^{-6} Torr of CO in Region D shows that the reactivated sample is able to absorb CO again.

However, the initial sticking probability is decreased to $S_0 \sim 0.2$.

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Fig. 1. Micrograph of the Al-Zr Surface.

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Fig. 2. The oxygen and carbon peak-to-peak heights as a function of the carbon monoxide pressure and the exposure time.

(PPPL-806462)

Fig. 3. Variations of carbon, oxygen, aluminum, and zirconium Auger peak-to-peak heights with exposure of Al-Zr to carbon-monoxide.

(PPPL-806492)

Fig. 4. The sticking probability as a function of surface coverage.

(PPPL-806491)

Fig. 5. The calculated S_r/S_m as a function of the groove angle.

(PPPL-806463)

Fig. 6. The variation of carbon and oxygen Auger peak-to-peak heights as a function of time during the course of the reactivation experiment.