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A STUDY OF THE KINETICS OF THE
INTERACTIONS OF CARBON MONOXIDE
AND OXYGEN WITH AL-Zr SURFACE

BY

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Introduction

In the previous work,¹ we reported on the study of CO adsorption on Al-Zr gettering material, which probably will be used in the TFTR (Tokamak Fusion Test Reactor) to control the density of hydrogenic plasmas² and to remove the chemically active gases such as carbon monoxide, oxygen, nitrogen, and water vapor. It is possible during the operations of the gettering pump that one of the active gases may change the surface structure and, consequently, it will block or inhibit the adsorption of the other gases and decrease the sticking probability and pumping speed. Therefore, we have carried out a study of the interaction of carbon monoxide and oxygen with an Al-Zr surface. The initial sticking probability of oxygen, the sticking probability as a function of doses of impurity contamination, and diffusion data have been measured.

Experimental

The apparatus used for this study and experimental procedure have been described in detail elsewhere.¹ Briefly, the apparatus consists of a PHI Scanning Auger Electron Spectrometer, an ultra high vacuum system which keeps the residual pressure in the main chamber below 5×10^{-10} Torr, a quadrupole mass spectrometer, and a UHV valve. The sample of Al-Zr (40/60 atomic percent) was provided by SAES Getters SPA Company. Ar^+ sputter cleaning produced a clean surface. For each measurement, the sample was cleaned by Ar^+ sputtering until the surface had the same atomic composition as the bulk atomic concentration. To minimize the surface contamination by residual gases which may affect the behavior of the gas adsorption, the Ar^+ gun was turned on until the surface was the same chemical composition as the bulk. At that moment the CO or O_2 gas was admitted through a UHV valve to the chamber and the Ar^+ gun was turned off. The pressure of the gas was measured by Bayard-Alpert ion gauge and the quadrupole mass spectrometer, both having been

calibrated with Baratron micromanometers to an accuracy of 10%. The purity of CO and O₂ gases as determined by the mass spectrometer were $> 98\%$.

Results and Discussion

1a. CO Adsorption on Oxygen Contaminated Al-Zr Surface.

Both the C and O Auger peak-to-peak heights have been monitored during the adsorption of CO on oxygen pretreated Al-Zr surface. It is found CO adsorption is very sensitive to oxygen contamination on the Al-Zr surface. A small amount of oxygen at the surface markedly reduced the amount of CO gas uptake and its sticking probability.

Finally, when the concentration of oxygen contamination equaled the saturation coverage of oxygen on clean Al-Zr surface, no CO adsorption was investigated.

Fig. 1 shows the oxygen uptake during the CO adsorption on the Al-Zr surface with different concentrations of oxygen contamination. The rate constant for uptake decreased remarkably with increasing oxygen concentration at the surface. The C uptake has the same rate constant as the oxygen uptake. Fig. 2 shows the saturation coverage of CO as a function of oxygen contamination at the Al-Zr surface. For example, 1.5×10^{14} molecule/cm² of oxygen contamination, the saturation concentration was reduced to 60% of the initial value.

1b. The Sticking Probability of CO(g) as a Function of Oxygen Contamination.

By using the relation $S = d\theta/dt \sqrt{2\pi mRT}/p$, where S is the sticking probability, $d\theta/dt$ is the increasing rate of coverage, p is the pressure. One obtains the initial sticking probabilities of CO(g) as a function of oxygen contamination at the Al-Zr surface, which is shown in Fig. 3. It is seen, that the initial sticking probability of CO decreased about a factor of 10

when the oxygen contamination was increased to a value $\sim 8.2 \times 10^{14}$ molecule/cm².

2a. O₂ Adsorption and Initial Sticking Probability.

The Auger peak-to-peak height of oxygen has been investigated during the exposure of Al-Zr samples to O₂ gas at 300 K. Fig. 4, shows the Auger peak-to-peak height for oxygen as a function of O₂ partial pressure and exposure time. It is seen that the oxygen uptake by the clean Al-Zr surface occurs in two distinct stages. First, there is rapid adsorption which leads to an initial saturation, followed by slow uptake of oxygen, which differs from the oxygen uptake in CO adsorption on Al-Zr. No linear increase on oxygen uptake has been found by O₂ adsorption. Using the same method as described in previous work, a saturation concentration of 1×10^{15} cm⁻² has been determined. From the initial slope for the oxygen uptake one obtains the initial sticking probability of oxygen on Al-Zr as $S_0 = 0.85$. The coverage dependent sticking probability is shown in Fig. 5. It can also be seen that the $S(\theta)$ curves for O₂ show a pronounced concavity, while those for CO do not. The initial sticking probability measured here is slightly higher than that of carbon monoxide.

2b. O₂ Adsorption on CO Contaminated Al-Zr Surface and the Initial Sticking Probability as a Function of CO Contamination on Al-Zr.

The uptake of oxygen on a CO contaminated Al-Zr surface as a function of CO coverage is shown in Fig. 6. It is seen that the oxygen adsorption is not very sensitive to pre-treatment of the clean Al-Zr surface with CO. The CO pre-treatment is not very effective at blocking the surface to subsequent O₂ adsorption. It is found that the O signal increased while the carbon signal decreased during exposure of CO contaminated Al-Zr to O₂(g). Fig. 7 shows the variation of the C signal during the O₂ adsorption on CO pre-treated Al-Zr.

The initial sticking probability of O_2 decreases slowly with increasing CO contamination. In spite of the concentration of the CO contamination, the final intensity of the C signal is about 50% of its original value. The saturation coverage of O as a function of CO contamination is shown in Fig. 8, and it is seen that the amount of oxygen uptake is not sensitive to the CO contamination. For example, the saturation coverage of O on Al-Zr with a contamination of $3.5 \times 10^{14} \text{ cm}^{-2}$ of CO is 30% less than that of a clean surface. The initial sticking probability of $O_2(g)$ on Al-Zr as a function of CO contamination is shown in Fig. 3.

3. Bulk Transport of Oxygen and Carbon:

Measurement of Atomic Diffusion Coefficient and Activation Energies.

By analysis of the depth profile of CO contaminated Al-Zr, it is found that there is transport of C and O atoms into the bulk even at room temperature. The transport of C and O atoms becomes more efficient at higher temperatures. Therefore, it is possible to investigate the diffusion behavior in quantitative detail. For this study, it is important that the diffusion investigation be carried out for the case where an oxide layer does not yet exist, or the exposure time of Al-Zr should be as short as possible to minimize the effect of the oxide layer on the diffusion behavior. From an analysis of the depth profile of the Al-Zr sample with different exposure time for the same pressure, it is found that the relations $\overline{AB} : \overline{AC} : \overline{AD} = \sqrt{1} : \sqrt{2} : \sqrt{8}$ exist. These results are shown in Fig. 9, and a relation has been deduced from Fick's Second Law of Diffusion.³

$$\left(\frac{\partial C}{\partial x}\right)_t = - \frac{C_s}{\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}},$$

where $(\partial C/\partial X)_\tau$ is the concentration gradient at time τ and depth X .

C_s is the saturation concentration, $C_s = 9 \times 10^{14}$ molecule/cm² which has been used for this evaluation.

D is diffusion coefficient. (cm² sec⁻¹).

The diffusion coefficient of C and O atoms as a function of temperature is shown in Fig. 10, and this leads to the following results:

$$D_C = 3.9 \times 10^{-15} \exp \left(-\frac{2200}{RT} \right) \text{ cm}^2 \text{ sec}^{-1}$$

$$D_O = 3.4 \times 10^{-15} \exp \left(-\frac{2500}{RT} \right) \text{ cm}^2 \text{ sec}^{-1}$$

The activation energies are: 2.2 Kcal/mol. for C atom and 2.5 Kcal/mol. for O atom.

Discussion

1. The measured initial sticking probability for oxygen is higher than that of carbon monoxide on Al-Zr. This result is in accordance with the results of the pumping speed measurement,⁴ the pumping speed for oxygen is higher than that for CO. It can be seen that the $S(\theta)$ curves for O₂ show a pronounced concavity towards the abscissa, while those for CO do not. It is known that the effects of surface heterogeneity can lead to this kind of curve for O₂.⁵ The other possible reason is that the adsorption of O₂ may involve the simultaneous interaction of both ends of the molecule with two adjacent vacant sites.⁵ In usual cases, the random two site adsorption will follow the relation $S(\theta) \sim (1 - \theta)^2$, from this the following relations can be obtained: $ds/d\theta \sim -2(1-\theta)$, and $d^2S/d\theta^2 \sim 2$. This indicates that the sticking probability decreases with increasing coverage and the curve is concave to the abscissa. The measured $S(\theta)$ curve provides a good fit to this relation.

2. The C signal decreased during exposure of the CO pre-treated Al-Zr to $O_2(g)$, the attenuation of the carbon signal may be due to: a) $CO(ad) + O(ad) \rightarrow CO_2(g)$. The adsorbed oxygen atom combines with the pre-adsorbed $CO(ad)$ to form carbon dioxide. b) $CO(ad) + O(ad) \rightarrow C(g) + 2O(ad)$, the C atom from the $CO(ad)$ is replaced by adsorbed $O(ad)$. c) Burial of the C atom below the surface during oxygen adsorption increased the escape depth of the Auger electron. The depth to which they are buried can be estimated by the following procedure. The ratio of the Auger intensity where the carbon is in the uppermost layer, $I(C)_O$, to the intensity with a layer of oxide, $\chi(\text{\AA})$, thick over the carbon atom, $I(C)_X$, is given by⁶

$$\frac{I(C)_O}{I(C)_X} = \exp\left(-\frac{\chi}{\lambda \sin\theta}\right),$$

where λ is the escape of the 272 eV (carbon) and $\sin\theta$ is the correction to λ for non-normal emission. From the results of the measurements the Auger signal ratio $I(C)_O/I(C)_X$ is about 2; with $\lambda = 8\text{\AA}$, gives a oxide layer thickness χ of 4.0 $\text{\AA}$ ($\theta = 45^\circ$). d) By changing the porosity of the surface during exposure to oxygen the diffusion coefficient of C atom is increased.

To distinguish between these possibilities, the following additional experiments have been done:

(1) The coverage of the Al-Zr pre-treated with CO, was always kept below the saturation coverage of the first stage of CO adsorption and then exposed to oxygen. The $m/e = 12$ and 44 have been monitored by a quadrupole mass spectrometer, but no change in intensity has been noticed within the sensitivity limit of the mass spectrometer.

(2) The clean surface has been exposed to 1×10^{-7} Torr of CO(g) for 20 sec, and then exposure to 1×10^{-7} Torr of $\text{O}_2(\text{g})$. Following this exposure, a depth profile for C has been done, these results are shown in Fig. 11. It is seen that the C atom has the highest concentration at a depth of $\sim 5\text{\AA}$. This value agrees reasonably well with the calculated oxide thickness. By comparison of the depth profile with different O_2 exposure, it is found: 1) The C Atom concentration in the bulk decreases with increasing O_2 exposure, 2) the C bulk concentrations beyond the peak are lower than that without O_2 exposure under the same experimental conditions. This finding indicates that the C atoms diffusion coefficient increases during exposure to O_2 . Therefore, it is reasonable to explain that the (a) increase in Auger electron escape length by the formation of an oxide layer and (b) changing the diffusion behavior of carbon in the bulk by exposure to oxygen caused the attenuation of the C signal at the surface.

3. In the previous work,¹ we reported the result of the measurement of the sticking probability of CO as a function of coverage, this is different from that of O_2 . It has been suggested that the CO adsorption is only the result of the interaction of the carbon end of the CO molecule with the surface. The oxygen end of CO interacts with the incident oxygen, in addition, our results tend to suggest that the part of C atoms is distributed as an underlayer during exposure to oxygen. From the above explanations, it is understandable why the CO contamination does not strongly affect the O_2 uptake as well as the sticking probability.

4. O_2 pre-treatment blocks the uptake of CO very effectively. The initial sticking probability decreased very rapidly with increasing O_2 contamination coverage. Therefore, a clean surface is essential for the accurate measurements of initial sticking probability of CO(g) .

5. By using the measured initial sticking probabilities of CO and O₂ on Al-Zr (40/60 atomic percent) for $S_{O,CO} = 0.71$ $S_{O,O_2} = 0.85$, the specific initial pumping speed at 300 K and 10^{-7} Torr is

$$V_{CO} = 7.6 \frac{\text{Liters}}{\text{Sec cm}^2}$$

and

$$V_{O_2} = 8.6 \frac{\text{Liters}}{\text{Sec cm}^2}.$$

Table I shows the specific pumping speed of CO as a function of oxygen contamination. It is seen that the pumping speed decreased very rapidly with O₂ contamination.

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Table 1. Specific Pumping Speed of CO as a Function of O₂ Contamination.

Oxygen Contamination	Specific Pumping Speed
(Torr sec)	of CO, v_{CO} (Liters/cm ² sec)
1×10^{-6}	5.4
2×10^{-6}	2.8
3×10^{-6}	1.1
4×10^{-6}	0.7

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Fig. 1. Oxygen intensity as a function of CO exposure with different concentrations of oxygen contamination.

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Fig. 2. CO saturation coverage as a function of oxygen contamination at the Al-Zr surface.

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Fig. 3. The initial sticking probability of CO and O_2 as a function of oxygen and carbon monoxide contamination at the Al-Zr surface.

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Fig. 4. Auger peak-to-peak height for oxygen as a function of O_2 partial pressure and exposure time.

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Fig. 5. The sticking probability of O_2 as a function of oxygen coverage.

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Fig. 6. The uptake of oxygen on a CO contaminated Al-Zr surface as a function of CO coverage.

Fig. 7. The variation of C signal during the O₂ adsorption on CO pretreated Al-Zr.

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Fig. 8. Saturation coverage of oxygen as a function of CO contamination.

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Fig. 9. Carbon depth profile as a function of exposure time.

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Fig. 10. The diffusion coefficient of C and O atoms as a function of temperature.

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Fig. 11. Carbon depth profile as a function of oxygen exposure for CO pretreated Al-Zr.