SURFACE INTERACTIONS OF IODINE WITH Fe_3O_4

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1

Introduction

The coolant circuit of high temperature gas cooled nuclear reactors contains fission product-iodine at very low partial pressure. The surface of the steel made ducts and heat exchangers consists mainly of a thin layer of Fe_3O_4 . Surface interactions of iodine at very low partial pressure with Fe_3O_4 at high temperature are of direct interest with regard to the mechanism that determine the transport and retention of fission product-iodine in the coolant circuit. This study is also of general interest because little quantitative information is available concerning the initial population of adatoms over the site distribution of oxide-surfaces. The work to be described is the determination of the population distribution of iodine on Fe_3O_4 powder as function of the initial coverage and the temperature during adsorption.

The two experimental techniques which have been used here are a pseudo-isopiestic method to expose Fe_3O_4 at high temperature to radioactive labelled gaseous iodine and thermodesorption to investigate the desorption of the adsorbed iodine into vacuum. The latter technique consists of heating a

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** Research sponsored by the Atomic Energy Commission under contract with the Union Carbide Corporation

sample at a linear rate and measuring the amount of iodine desorbed. The analyses of the resulting desorption rate curve can provide the order of the reaction and the activation energy of desorption. Methods for analyzing thermal desorption experiments were examined particularly by Smith and Aranoff [1], Ehrlich [2], Redhead [3], Carter [4], and McCarroll [5]. Most of the experimental work has been done with metal filaments. Czanderna [6] has used a microbalance technique to study desorption of gases from silver powder into vacuum and Cvetanovic and Amenomiya [7] studied desorption of gases adsorbed on oxide powders into a carrier gas stream. A radioactive tracer technique was employed by Oishi and Iwamoto [8] to investigate the release of barium from graphite powder.

2 Experimental

The Fe_3O_4 used was prepared by oxidizing carbonyl Fe-powder with flowing steam containing a small amount of hydrogen. The reaction was carried out at temperatures between 245 and 500°C for several days. The resulting sintered oxide was ground to 100 mesh. Chemical analyses along with the spectrographic check for impurities and the determination of lattice constant and density indicated that the material was truly Fe_3O_4 . The sum of the

impurities was less than 0.2 %. The details of the characterization are given in a paper by Sweeton and Baes [9], who kindly supplied the Fe_3O_4 used in this study. The specific surface area was determined by the adsorption of krypton using the B.E.T. method as $0.16 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$. Prior to the krypton-adsorption the samples were degassed in vacuum at 400°C .

Solid iodine labelled with I^{131} -tracer was prepared by thermal decomposition of PdI_2 at 350°C . The latter was obtained using a method by Carroll [10]. An excess of concentrated PdCl_2 -solution was added to a solution of ~100 mg NaI tagged with up to 20 mCi I^{131} . Saturated H_3PO_3 was used to reduce the palladium-ions remaining in solution. The resulting mixture of PdI_2 and Pd was thoroughly washed with distilled water and dried at 250°C in vacuum. Prior to the precipitation three samples of the tagged NaI-solution were taken and the iodine concentration was measured by potentiometric titration. One sample of known iodine content was used later as a standard to determine the amount of iodine adsorbed on the Fe_3O_4 . The quartz tube containing the PdI_2 -Pd was fused to a small all glass apparatus which was evacuated by a liquid nitrogen trapped pump. The PdI_2 -Pd was heated to 300°C for degassing while the apparatus was baked at 400°C . Degassing was finished after about an hour when visible traces of iodine appeared at the trap. Finally the apparatus was fused off and the PdI_2 -Pd was slowly

heated to 350°C . The evolving iodine first sublimed into a tube cooled by liquid nitrogen. By allowing a very slow warm-up of this tube the iodine migrated to a cooled breakseal tube which was sealed off. This breakseal tube provided the iodine source for the experiments.

A pseudo-isopiestic technique to expose metals at high temperature to iodine at low partial pressure was used by Zumwalt et al. [11]. The all-glass apparatus employed in this study is shown in fig. 1. The Fe_3O_4 -powder ($\sim 2\text{ g}$) was situated on a rotating quartz-plate. The elemental iodine was contained in a breakseal tube. The apparatus was linked to a liquid nitrogen-trapped mercury diffusion pump via the greaseless glass ground joint 1 by means of a viton-O-ring connector. Initially the cooling bath shown was replaced by a heating mantle. Then the apparatus was baked at 400°C with the ground joints 1 and 2 open for at least two days until a pressure of 3×10^{-5} torr was maintained for several hours when the heating was being continued with the apparatus closed-off from the pumps. After bake-out the ground joints were magnetically closed, however the vacuum pumps were kept running. To start an adsorption experiment, the dewar vessel containing a mixture of dry ice and CHCl_3 was installed and the temperature of the heated part of the apparatus was adjusted to the desired value. The iodine ampoule was cooled to -75°C when the breakseal was

broken. By allowing a slow warm up of this ampoule the iodine migrated into the tube which was refrigerated by CHCl_3 - CO_2 -slush. Adsorption commenced when ground joint 2 was opened magnetically. The iodine pressure at -75°C is 7.6×10^{-7} torr [12]. Iodine adsorption was followed continuously by means of suitably shielded γ -scintillation counter. The duration of one experiment was ~ 10 hours. Finally, the quartz plate carrying the Fe_3O_4 was turned magnetically in order to transfer the powder in vacuo into the five breakseal tubes which were sealed-off. The amount of iodine adsorbed was determined by measuring the I^{131} -activity of each Fe_3O_4 -sample and of a sample of NaI-solution of known iodine content mentioned above. The loss of countrate due to self-shielding of the Fe_3O_4 was taken into account. The error of the determination of the iodine loading as estimated from the spread of five measurements was usually less than $\pm 5\%$. The systematic error due to the error of the specific surface area is not included in the uncertainties given in the table.

The kinetics of desorption into vacuum were measured using a quartz apparatus (see fig. 2) consisting of a spherical desorption chamber between two large liquid nitrogen cooled traps. The latter serve as cryopumps and provide an almost infinite pumping speed for the slowly desorbing iodine.

Desorption curve Number	T_A ($^{\circ}\text{C}$)	N_0 (I-atoms cm^{-2})	b ($^{\circ}\text{K sec}^{-1}$)	T_M ($^{\circ}\text{C}$)	R_M (I-atoms $\text{cm}^{-2} \text{sec}^{-1}$)
1.1	250	$(4.54 \pm 0.29) 10^{12}$	2.25×10^{-2}	460 ± 10	6.51×10^8
2.1		$(4.67 \pm 0.23) 10^{13}$	2.41×10^{-2}	375 ± 10	6.75×10^9
3.1		$(9.8 \pm 0.5) 10^{13}$	2.32×10^{-2}	350 ± 10	1.4×10^{10}
4.1		$(4.10 \pm 0.07) 10^{14}$	2.23×10^{-2}	342 ± 5	7.91×10^{10}
1.2	250	$(4.54 \pm 0.29) 10^{12}$	1.80×10^{-1}	500 ± 10	4.80×10^9
3.2		$(9.8 \pm 0.5) 10^{13}$	1.7×10^{-1}	385 ± 10	1.08×10^{11}
4.2		$(4.10 \pm 0.07) 10^{14}$	1.72×10^{-1}	395 ± 10	4.28×10^{11}
5	350	$(3.68 \pm 0.05) 10^{13}$	2.06×10^{-2}	430 ± 10	6.91×10^9
6	450	$(3.54 \pm 0.33) 10^{13}$	2.12×10^{-2}	428 ± 5	7.72×10^9

T_A temperature during adsorption, N_0 initial coverage, b linear heating rate,
 T_M temperature at maximum desorption rate, R_M maximum desorption rate

Prior to a desorption experiment the apparatus was baked at 400°C. The residual gas pressure was measured by a Bayard-Alpert-gauge. A breakseal tube containing iodine loaded Fe_3O_4 was inserted into the desorption chamber and locked in the position shown in fig. 2. The traps were filled with liquid nitrogen when the apparatus was evacuated to 10^{-7} torr. To start a desorption experiment the tube was moved down magnetically and the breakseal was broken. The Fe_3O_4 -powder was distributed as a layer of about 0.2 mm thickness on the quartz plate in the center of the desorption chamber. The empty breakseal tube was moved up and fixed at its former position. The specimen temperature was raised at a constant average rate and was measured by two chromel-alumel-thermocouples made from 0.1 mm wire. Only the bead placed in a well in the quartz plate was bare, the wire was protected by alumina tubing. One thermocouple was used to record the temperature, the other one was employed to drive a Leeds and Northrup-three mode temperature controller with self-saturable reactor combined with a sweep-generator. The difference between the real temperature as recorded by the thermocouple and the temperature corresponding to an exact linear increase with time was within $\pm 1\%$ of the latter. The decrease of the activity of the ^{131}I -tracer was measured automatically by ORTEC- γ -counting equipment consisting of a single channel analyzer and a suitably shielded γ -scintillation

crystal which was situated beneath the desorption chamber. A computer code was used to process the data which were produced as punched tape. In order to check the reproducibility each experiment was repeated once using an other Fe_3O_4 -sample.

3 Results

Iodine loaded Fe_3O_4 -samples with four different initial coverages were prepared at 250°C and two heating rates differing by a factor of ~ 10 were used in the desorption experiments. At 350 and 450°C Fe_3O_4 -samples were exposed to gaseous iodine until about the same initial coverage was obtained and one heating rate only was employed to measure the desorption. Each of the desorption rate curves displayed in figures 3, 4, and 5 consists of the data of two different experiments, except curve 4.2. The data were smoothed to reduce the effect of random errors. Then a curve was drawn through the points and judged for best fit visually. The error bars indicate the probable error due to the counting statistics when the ^{131}I -activity of the specimen was measured. At room temperature the desorption rate was zero throughout. The table lists the temperature during adsorption, T_A , the initial coverage, N_0 , the average linear heating rate, b , the temperature at maximum desorption rate, T_M , and the maximum desorption rate, R_M .

Fig. 3 shows desorption curves obtained on heating Fe_3O_4 after its exposure to iodine at 250°C . The heating rate was $\sim 1^\circ\text{K/min}$. The initial coverage N_0 increased from curve 1.1 to 4.1. The curves shown in fig. 4 were obtained on heating samples of the same iodine loaded Fe_3O_4 which was used in case of the spectra displayed in fig. 3, however, the heating rate was $\sim 10^\circ\text{K/min}$. The Fe_3O_4 -samples used to obtain the desorption curves 2.1, 5, and 6 shown in fig. 5 were loaded to approximately the same initial coverage at 250 , 350 , and 450°C , respectively. The heating rate was $\sim 1^\circ\text{K/min}$.

The results of the desorption experiments may be summarized as follows: the desorption curves contained only a single peak for $N_0 \leq 10^{14}$ (I-atoms/ cm^2), but three peaks occurred for $N_0 = 4 \times 10^{14}$ (I-atoms/ cm^2). For the lower heating rate desorption ceased independently of T_A and N_0 at 550°C and at 600°C for the higher heating rate. There was a marked shift of T_M toward lower temperatures as N_0 increased from 5×10^{12} to 10^{14} (I-atoms/ cm^2). A further increase of N_0 did not cause an additional decrease of T_M the temperature at maximum desorption rate. Thus, T_M became independent of the initial coverage. For constant N_0 the temperature range of desorption decreased with increasing T_A .

Discussion

Provided re-adsorption is negligible the desorption rate is given by

$$-\frac{dn_i}{dt} = \gamma n_i^\alpha \exp(-E_i/RT) \quad (1)$$

where n_i is the number of atoms per cm^2 , t is the time, γ is the rate constant, E_i is the activation energy of desorption, R is the gas constant, T is the temperature in $^\circ\text{K}$ and α is order of the reaction.

In this study the temperature was raised at a constant rate

$$T = T_0 + bT \quad (2)$$

Considering desorption from sites with singular activation energy, the rate curves for first- and second-order differ in shape and in their dependence on the initial coverage N_0 [1 - 5]. Only the second-order curve is symmetric about the maximum and is shifted toward lower temperatures as N_0 is increased. Only the first-order desorption terminates at the same temperature and T_M is independent on N_0 . Assuming the same desorption energy and rate constant, second-order peaks are broader than first-order peaks. Some of the curves obtained here look like those for

first- or second-order desorption from sites with singular activation energy, but the width of the peaks depends strongly on the temperature during iodine adsorption. Fig. 6 displays again desorption rate curve 6 along with some calculated curves for first-order (thin lines) and one for second-order (circles) assuming $\gamma = 10^{13} \text{ sec}^{-1}$. The experimental curve 6 could be well fitted assuming second order kinetics from sites with singular desorption energy since the choice of a smaller γ would increase the peak width of the calculated curve [13]. In case of the desorption rates obtained on heating Fe_3O_4 after its exposure to iodine at 250°C however, the width of the peaks was much broader than one ever could expect for desorption from monoenergetic sites even in case of a second-order process. Consequently, it was concluded that iodine was released from sites of many differing binding energies. A distinction between first- and second-order is not possible unless additional information is available. It is probably justified to assume the distribution at equilibrium of the adsorbed iodine over the various surface sites because of the high temperature and the long time of exposure. The iodine would then adsorb preferentially on the strongest sites. In that case T_M would decrease as N_o increases for both, first- and second-order desorption. However, the experimental result that T_M became independent of N_o at

higher initial coverage and that desorption terminated at the same temperature regardless of the initial conditions can be explained only if desorption was first-order. Thus, iodine desorption from Fe_3O_4 was taken as a first-order process.

There was obviously no penetration of iodine into the bulk along grain boundaries. Such a process would be strongly dependent on T_A , the temperature of the Fe_3O_4 during its exposure to iodine. The diffusion-controlled release of iodine would cause a "tail" in the desorption spectrum. For a given N_0 and heating rate, the temperature at which desorption terminates would then increase with increasing T_A .

The release of adsorbed atoms with slightly different desorption energies E_i causes overlapping of adjacent peaks. Resolution increases as the heating rate decreases. Considering a heating rate of $1^\circ\text{K}/\text{min}$ and the independent first-order release of adsorbed atoms with E_1 and E_2 two adjacent peaks of about the same height should be resolved if $E_1 - E_2 \gtrsim 2.5 \text{ kcal/mole}$. The desorption rate curves obtained here showed no distinct peaks, except for the highest initial coverage. It is therefore justified to assume for the further evaluation a continuum of desorption energies.

The initial site population as function of the desorption energy was determined assuming that the measured desorption rate curve was the sum of independent first-order desorption processes. The rate constant γ was set at 10^{13} sec^{-1} . A computer code was utilized to solve the corresponding set of linear equations for the number of atoms n_{i0} initially adsorbed on sites possessing desorption energy E_i . This method was proposed and used before by Carter [4] and is outlined briefly below.

For first-order desorption and a linear heating rate the solution of eq. (1) is:

$$n_i(T) = n_{i0} \exp \left[- \frac{\gamma}{b} \int_0^T \exp(-E_i/RT) dT \right] \quad (3)$$

where n_{i0} is the initially present number of atoms per cm^2 desorbing with E_i .

The overall desorption rate is

$$\frac{dN}{dt} = \sum_i x_i \frac{dn_i}{dt} \quad \text{where} \quad (4)$$

$$x_i = \frac{n_{i0}}{N_0} \quad \text{and} \quad N_0 = \sum_i n_{i0} \quad (5)$$

For temperatures between T_1 and T_k a system of linear equations results:

$$\begin{aligned} x_1 \left(\frac{dn_1}{dt} \right)_{T_1} + \dots + x_i \left(\frac{dn_i}{dt} \right)_{T_1} + \dots + x_k \left(\frac{dn_k}{dt} \right)_{T_1} &= \left(\frac{dN}{dt} \right)_{T_1} \\ x_1 \left(\frac{dn_1}{dt} \right)_{T_2} + \dots + x_i \left(\frac{dn_i}{dt} \right)_{T_2} + \dots + x_k \left(\frac{dn_k}{dt} \right)_{T_2} &= \left(\frac{dN}{dt} \right)_{T_2} \\ x_1 \left(\frac{dn_1}{dt} \right)_{T_k} + \dots + x_i \left(\frac{dn_i}{dt} \right)_{T_k} + \dots + x_k \left(\frac{dn_k}{dt} \right)_{T_k} &= \left(\frac{dN}{dt} \right)_{T_k} \end{aligned} \quad (6)$$

Values of the integral in eq. (3) were calculated using a power series for approximation [1]. The Gauss-Seidel-method was employed to solve the equations for the x_i . The energy spectrum was divided into intervals $\Delta E = E_{i+1} - E_i = 1.75$ kcal/mole. x_i is then the fraction of atoms desorbing with approximately $E_i \pm \Delta E/2$. After the determination of the n_{i0} the overall desorption rate curve was calculated by superposition of the weighted individual rate curves. This calculated curve was compared to the measured one. For all initial site populations shown later the calculated and the curve drawn through the smoothed measured desorption rates agreed within $\pm 1\%$.

For $E_i \geq 30$ kcal/mole the system of equations became ill-conditioned when the energy spectrum was divided into finer intervals than 1.75 kcal/mole. It is then difficult to find a numerical solution and it will be of doubtful accuracy. The code was tested using computer simulated desorption curves with known n_{i0} . It was found that the accuracy of the calculated n_{i0} was sensitive to experimental errors as would be expected. For instance, if 20 unknowns were to be calculated, a random error of $\pm 5\%$ for the measured rates prevents a reasonable solution.

The results of the analyses of the desorption rate curves 1.1 through 6 (see table) are displayed in fig. 7, 8, and 9. Fig. 7 and 8 show the energy spectra calculated from rate curves obtained on heating Fe_3O_4 after its exposure to gaseous iodine at $T_A = 250^\circ\text{C}$. The circles and filled circles represent data for the high and low heating rates, respectively. There is agreement between the initial populations calculated from desorption curves measured for heating rates differing by a factor of about 10. This seems to prove that re-adsorption of desorbing iodine or its re-distribution on the surface during the desorption experiments was negligible. Fig. 9 is a similar plot obtained by analyzing the rates of desorption of iodine adsorbed on Fe_3O_4 at T_A equal to 350°C (circles) and 450°C (triangulars).

The energy spectra shown in fig. 7 refer to initial coverages of 4.54×10^{12} (bottom), 4.67×10^{13} (center) and 9.8×10^{13} (1-atoms/cm²),

i. e. N_0 increases in the order given. The maximum of the energy spectrum, that is, the most frequently occurring desorption energy was shifted toward lower energies as N_0 increased. However, the range of the desorption energies was independent of N_0 . Thus, different sites filled during adsorption simultaneously. Comparison with fig. 9 shows that many sites with lower binding energies were not occupied when T_A was 350 or 450°C. The curves shown in fig. 7 and 9 were calculated according to (7):

$$\frac{x_i}{\Delta E} = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-\frac{(E^j - E_i)^2}{2 \sigma^2} \right] \quad (7)$$

where E^j is the average desorption energy and σ is the standard deviation.

Equation (7) is the mathematical description of a Gaussian-distribution of desorption energies. It follows that at low initial coverages the actual distribution of desorption energies may be more or less well described by a Gaussian function.

It should be mentioned that Ross and Olivier [14] assume the normal probability curve to be applicable as a general description of substrate heterogeneity. Comparing the energy spectrum for $N_0 \approx 10^{14}$ (fig. 7, top) to that for $N_0 \approx 4 \times 10^{14}$ (I-atoms/cm²) (fig. 9) it is surprising that the shape of the spectrum changes so much as the coverage increases by a factor of 4, whereas at lower coverages an increase of N_0 by a factor of 25 causes only a shift of the maximum to lower energies. One explanation could be, that iodine molecules populate the surface too as higher coverages are approached and desorb with a desorption energy of 1.95 eV. McCarroll [15] has investigated surface interactions of iodine vapour with tungsten using a mass-spectrometer and found at higher coverages first order desorption of iodine-atoms and -molecules. The iodine molecule desorption energy was about 1.8 eV.

Acknowledgements

The author wishes to acknowledge the facilities granted by Oak Ridge National Laboratory for the pursuit of this work and discussions with the staff of the reactor chemistry division. I am especially grateful to Dr. H. J. de Nordwall for discussions and to Dr. 's C.F. Baes und F. H. Sweeton for supplying the Fe_3O_4 used in this study. The authors stay at ORNL was supported by a grant of the Bundesministerium für Bildung und Wissenschaft, Bonn.

References

- [1] Smith, A. W. J. Phys. Chem. 62 (1958) 684-686
Aranoff, S.
- [2] Ehrlich, G. J. Appl. Phys. 32 (1961) 4-15
- [3] Redhead, P. A. Vacuum 12 (1962) 203-211
- [4] Carter, G. Vacuum 12 (1962) 245-254
- [5] McCarroll, B. J. Appl. Phys. 40 (1962) 1-9
- [6] Czanderna, A. W. Vacuum Microbalance Technique
Vol. 6 (1967) p. 129
Ed. A. W. Czanderna
Plenum Press, New York
- [7] Cvetanovic, R. J. Advances in Catalysis 17 (1967) p. 103-149
Amenoniy, Y. Academic Press, New York
- [8] Iwamoto, K. J. Nucl. Mat. 29 (1969) 285-301
Oishi, J.
- [9] Sweeton, F. H. J. Chem. Thermodynamics 2 (1970) 479-500
Baes, C. F., Jr.
- [10] Carroll, S. T., Jr. Private Communication
- [11] Zumwalt, L. USAEC Report
Anderson, E. GA-3053 (1962) 74-75
Busch, D.
Moses, H.
Snow, W.

- [12] Honig, R.E. RCA-Review 21 (1960) 360
Hook, H.O.

- [13] Czanderna, A.W. J. Colloid. Interf. Sci. 34 (1970) 406-412
Biegen, J. R.
Kollen, W.

- [14] Ross, S. On Physical Adsorption
Olivier, J.P. Wiley-Interscience, New York, 1964

- [15] McCarroll, B. J. Chem. Phys. 47 (1967) 5077-82

Figure captions

- 1 Adsorption apparatus
- 2 Desorption apparatus
- 3 Desorption rates obtained on heating Fe_3O_4 -powder after its exposure to gaseous iodine at 250°C . The linear heating rate was about $1^\circ\text{K}/\text{min}$. The initial coverage increased from curve 1.1 to 4.1. The numbers refer to the table. The data of two experiments are shown for each curve.
- 4 Desorption rates obtained on heating Fe_3O_4 -powder after its exposure to gaseous iodine at 250°C . The linear heating rate was about $10^\circ\text{K}/\text{min}$. The initial coverage increased from curve 1.2 to 4.2. The numbers refer to the table. The data of two experiments are shown for each curve, except for 4.2.
- 5 Desorption rates obtained on heating Fe_3O_4 -powder after its exposure to gaseous iodine at 250°C (curve 2.1), 350°C (curve 5), and 450°C (curve 6). The linear heating rate was about $1^\circ\text{K}/\text{min}$. The initial coverage was about the same for all curves. The data of two independent experiments are shown for each curve. The numbers refer to the table.
- 6 The measured desorption rate curve number 6 along with some first order-(thin lines) and one second order-curve (circles) for desorption from monoenergetic sites. τ was set to 10^{13} sec^{-1} .

- 7 Energy spectrum determined from desorption rate curves 1.1 and 1.2 (lower), curve 2.1 and curves 3.1 and 3.2 (upper). The initial coverage decreased in the order given. The filled circles refer to lower heating rate. The curves correspond to a Gaussian-distribution of desorption energies.
- 8 Energy spectrum determined from desorption rate curves 4.1 (filled circles) and 4.2. The temperature during iodine exposure was 250°C .
- 9 Energy spectrum determined from desorption rate curves 5 (circles) and 6 (triangulars). The temperature during iodine exposure was 350°C and 450°C , respectively. The curves correspond to a Gaussian-distribution of desorption energies.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9