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Kinetics of water vapour absorption on evaporated iron and titanium films

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Abstract

The absorption kinetics of water vapour on evaporated Fe and Ti films has been studied by means of quartz-crystal microbalance measurements. The quartz-crystal microbalance technique is uniquely suitable to follow continuously the absorption kinetics at moderate temperatures from ultrahigh vacuum to atmospheric pressures. It is more sensitive to the uptake of oxygen than of hydrogen. The reaction between water vapour and evaporated iron and titanium films of 60 nm thickness has been investigated at 80°C at 1×10^{-4} mbar. The partial pressures of the components of the residual gas in the vacuum chamber have been continuously controlled. The absorption kinetics is compared to the initial absorption rate of oxygen from O_2. A fast initial absorption step found with O_2 has not been observed with both metals. In the case of Fe the absorption is strongly delayed, remarkable mass uptake has been observed several minutes, in some cases even hours after water vapour exposure started. For Ti the oxygen absorption begins immediately with the exposure, but the initial absorption rate is smaller than for oxygen gas. The results are compared to those obtained by the volumetric method for H_2O and O_2.

Keywords: Fe; Ti; H_2O; Absorption kinetics; Quartz-crystal microbalance

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1. Introduction

The experimental investigation of the absorption kinetics of gases on clean metal surfaces at near room temperature is difficult because very thin absorption layers have to be measured with high resolution and precoverage of the surface with possible contaminating specii must be avoided. The most commonly used surface analysis methods (e.g., Aüger electron spectroscopy, X-ray photon spectroscopy, or secondary ion mass spectroscopy) providing information about the structure and chemical composition of the absorption layer are restricted to very low pressures. They detect only the topmost absorption layers with high accuracy and are not suited for continuous measurement of the absorption kinetics.

The volumetric method that yields the reaction probability of the gas–metal reactions is in its original form [1] especially appropriate for the investigation of hydrogen absorption of metals. The early stages of oxidation or the effects of surface contamination on hydrogen absorption have also been successfully investigated by this method [2,3]. Additional thorough analysis of the total and the partial pressures measured makes the method applicable to investigate even more complex gas–metal reactions, such as H_2O decomposition on surfaces [4,5]. However, for reliable quantification the possible side effects caused, e.g., by the hot filaments of the pressure gauges must also be considered.

The piezoelectric quartz-crystal microbalance technique offers a sensitive direct and continuous measurement of the amount of absorbed gas at moderate temperatures up to atmospheric pressures and has already been used for the investigation of the initial oxidation kinetics of evaporated metal films [6]. The application of the method for the investigation of the absorption of water vapour on metal surfaces enables the comparison of the initial oxidation behaviour in pure oxygen gas and in water vapour and can contribute to the understanding of the interaction of water vapour with metals which is of fundamental interest.

In the present work results on the absorption kinetics of H_2O and O_2 on evaporated iron and titanium films obtained by quartz-crystal gravimetry are reported and are qualitatively compared to those obtained by the volumetric method.

2. Experimental

The quartz-crystal microbalance measurements have been taken in a highly sophisticated temperature stabilized system. Standard 6 MHz AT-cut quartz crystals with gold electrodes have been used performing with a sensitivity of

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8.13×10^6 Hz m^2 kg^{-1}, i.e., 0.23 ML O_2 Hz^{-1} and 0.41 ML H_2O Hz^{-1}, respectively (1 ML=1 monolayer$\equiv10^{15}$ molecules cm^{-2}). The quartz is suspended on the thin leads of the high frequency supply and on the thermocouple fixed to the quartz by two-component conductive silver glue. The quartz is heated by an infrared lamp and its temperature is stabilized better than ±0.1°C. The stability of the quartz frequency is better than ±0.5 Hz within one day, the longtime stability is ±8 Hz. The vacuum system, the quartz-crystal microbalance arrangement, and the experimental procedure with pure oxygen are described in more detail elsewhere [7].

Titanium and iron films (60 nm thick) were evaporated at a rate of 3 nm min^{-1} in ultrahigh vacuum of 2×10^{-8} mbar from resistivity heated pure metal bars. Distilled water carefully degassed by a repeated freezing–evacuating–thawing procedure was introduced into the reaction chamber about 20–40 min after the film evaporation. The system was then thermally equilibrated again which was indicated by the stable quartz frequency. In order to reduce the sedimentation on the gas inlet valve and on the receiver wall, the valve opening and the vacuum chamber wall were kept at 60°C. The measurements were performed at $p_{H_2O} = 1\times10^{-4}$ mbar in a steady-state pressure mode. Besides the control of the total pressure also the partial pressures in the reaction chamber were recorded.

During the experiments, the partial pressure of water vapour increased more slowly than the total pressure consisting of mainly the partial pressure of H_2. Keeping the total pressure constant it took about one hour till the H_2O partial pressure reached the stable value of 10^{-4} mbar. Fastest gas admission within about 10 min could be attained by paying attention only to the terminal value of p_{H_2O}.

3. Results

3.1. Iron–H_2O

Fig. 1 shows typical mass gain curves of iron films in oxygen and in water vapour measured by the quartz-crystal microbalance method. The lower part of the figure shows the partial pressures of the residual atmosphere in the course of the H_2O measurement. The mass uptake during H_2O exposure shows an extended initial delay of at least some ten minutes. A fast initial oxidation step as typical with O_2 exposure, where a 15 monolayer thick oxide layer is formed, was not observed. After the onset of perceptible mass uptake the rate of mass gain is higher than that for O_2. Although the H_2O partial pressure increases slowly in the receiver it cannot be made responsible for the observed inhibited mass gain. The measurement was taken at relatively fast water vapour admission. No remarkable change in the absorption kinetics has been observed for slow water vapour admission.

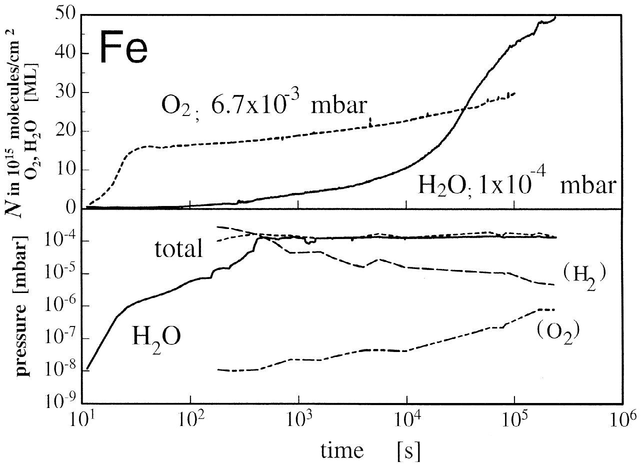

Fig. 1. Mass gain kinetics for iron films at 80°C in O_2 and in H_2O. Total pressure and partial pressures in the reaction chamber during water vapour absorption.

3.2. Titanium–H_2O

In the upper section of Fig. 2 mass gain vs. log t curves measured by the quartz-crystal microbalance technique in O_2 (dashed line) and in water vapour (solid line) are shown. The lower part of the figure presents the total pressure and the H_2O partial pressure during the measurement. Here again the lack of a fast initial reaction step is evident which is characteristic for the oxidation kinetics in O_2 gas. Compared with iron the H_2O curve indicates a somewhat different behaviour. Mass gain is observed as soon as the partial pressure of H_2O increases. Since the oxidation of titanium shows a remarkable pressure dependency also in H_2O, the data of the initial part of the measurement cannot be evaluated more precisely.

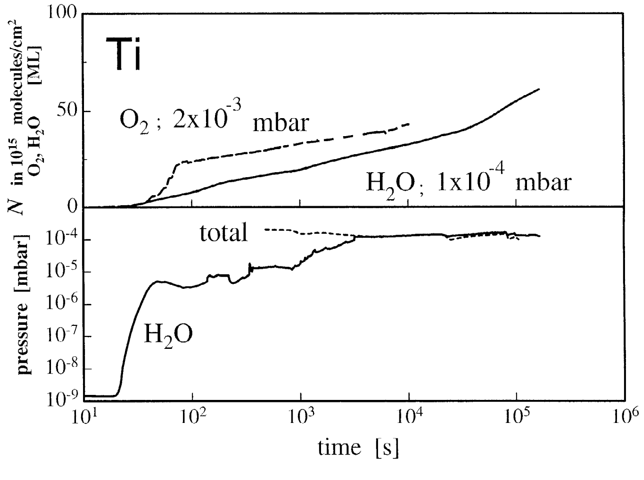

Fig. 2. Mass gain kinetics for titanium films at 80°C in O_2 and in H_2O. Water vapour partial pressure and total pressure in the reaction chamber during water vapour absorption.

4. Discussion

4.1. Fe–H_2O

The delayed mass uptake observed by quartz-crystal microgravimetry on iron films exposed to water vapour is in agreement with the general opinion, that iron shows a lower reactivity with water than with O_2. It is commonly observed that water vapour forms with pure iron surfaces hydroxyl-containing groups which passivate the surface. This can explain the differences in reaction kinetics between the iron–water and the iron–oxygen reaction [8,9].

After dissociation of the H_2O molecules on the metal surface hydrogen atoms can either be absorbed or desorbed as hydrogen gas molecules. Since the quartz-crystal microbalance method is less sensitive to the uptake of the light hydrogen atoms, the results provided by the volumetric method for H_2O, O_2 and H_2 are helpful for the discussion. In Fig. 3 the reaction probability for H_2O, r_{H_2O}, on an iron film at 300 K is plotted as a function of the number of reacting molecules, N_{H_2O}. For comparison also reaction probabilities are shown for hydrogen, r_{H_2}, and for oxygen, r_{O_2}, measured in H_2 and O_2 gas, respectively, at 300 K. The analysis of the partial pressures makes it possible to define the probability of hydrogen absorption from H_2O, $r^*_{H_2}$, [5,10].

During the reaction of iron films with H_2O the initial probability of H_2O dissociation is unity. All impinging molecules dissociate and hydrogen and oxygen atoms are absorbed simultaneously. Enhanced absorption of hydrogen atoms produced by the dissociation of H_2O is observed when compared to the absorption from H_2 gas. The initial plateau at $r_{H_2O} = 1$ is, however, only about two monolayers long, much shorter than the 10 monolayers for oxygen atoms absorbed in O_2 gas. The lack of a fast initial step in the mass gain curve in Fig. 1 demonstrates the reduced reactivity of the iron film to water vapour compared to O_2 gas. For higher coverages the reaction probabilities r_{H_2O} and r_{O_2} decrease about exponentially and parallel to each other. Also the growth of the absorption layer in the gravimetric measurement shows similar rates in H_2O and in O_2. Simultaneously to the decrease of the reaction probability, an increase of p_{H_2O} and p_{H_2} in the receiver was found in the volumetric measurement with water vapour, indicating that part of the hydrogen atoms produced by the dissociation of the H_2O molecules desorbs as hydrogen gas molecules. The fact that not all hydrogen atoms from the H_2O molecules are desorbed as H_2 gas molecules, can be taken as an evidence for formation of a hydroxide layer on the surface. The present arrangement of our quartz-crystal microbalance system is not yet optimally suited for accurate gas analysis that could support this conclusion in a more quantitative manner. The almost constant value of r_{H_2O} in the latest stage of the reaction in Fig. 3 is reflected by a steeper mass gain curve observed by the quartz microbalance technique (Fig. 1).

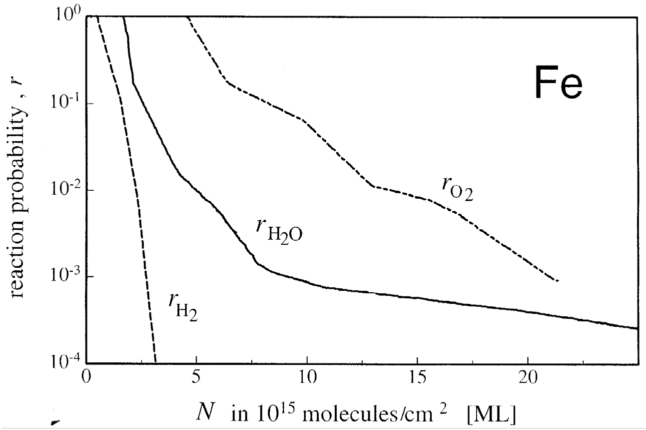

Fig. 3. Reaction probabilities of H_2O, H_2 and O_2 vs. amount of absorbed molecules for a 20 nm thick iron film at 300 K [5,10]. The plateau length with respect to oxygen atoms is $2N_{O_2}$.

Experiments similar to those presented here have been reported in Ref. [11] where a 10 MHz AT-cut quartz with a sensitivity of 2.12×10^{-9} g cm^{-2} Hz^{-1} was used for measurements of the uptake kinetics of 10 nm thick evaporated iron films in pressures in the range of 5×10^{-7} to 4×10^{-5} torr. An undelayed mass uptake for H_2O is reported but sticking coefficients orders of magnitude lower for H_2O than for O_2 were found also there.

4.2. Ti–H_2O

The mass uptake of titanium films measured by the quartz-crystal microbalance method during water vapour exposure shows no initial fast oxidation step and its rate is comparable to the second, slower part of the oxidation kinetics in O_2. Since the height of the initial step in O_2 is pressure dependent [6], suppression of a fast oxidation step by measuring the mass uptake at low water vapour partial pressure can not be entirely excluded.

In Fig. 4 the reaction probability for H_2O, r_{H_2O}, on a titanium film at 300 K is plotted as a function of the number of reacting H_2O molecules, N_{H_2O}. The reaction probabilities r_{H_2} and r_{O_2} vs. N_{H_2} and N_{O_2} measured in H_2 and O_2 gas, respectively, are also shown. Hydrogen atoms produced by the dissociation of H_2O are more easily incorporated into the metal surface than those of hydrogen gas due to the non-activated chemisorption of the H_2O molecule on the metal surface. It holds that $r^*_{H_2} \approx r_{H_2O}$ which means that most of the hydrogen evolving by the dissociation of H_2O is absorbed. In the case of Ti simultaneous H_2 solution or hydride formation and O_2 absorption is possible. The length of the initial plateau at $r_{H_2O} = 1$ is only half as long as for oxygen if the amount of absorbed oxygen is given in atoms and not in molecules O_2 [10]. This also contributes to the observation that no

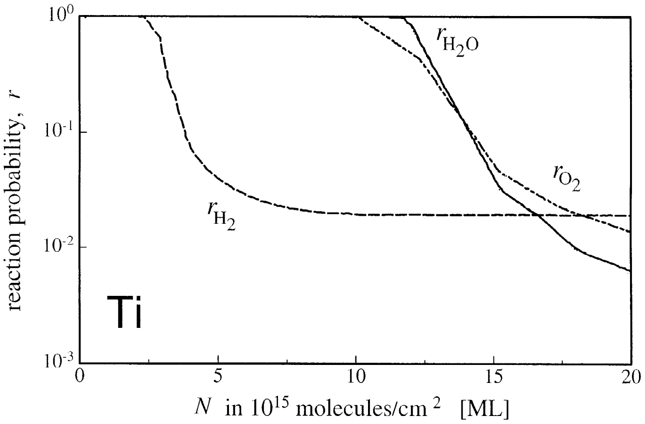

Fig. 4. Reaction probabilities of H_2O, H_2 and O_2 vs. amount of absorbed molecules for a 30 nm thick titanium film at 300 K [10]. The plateau length with respect to oxygen atoms is $2N_{O_2}$.

fast initial step is seen in the mass uptake (Fig. 2). The similar slope of the exponential decrease of r_{H_2O} and r_{O_2} subsequent to the plateau (Fig. 4) is in good agreement with the parallel course of the mass gain kinetics in Fig. 2.

5. Conclusions

The results obtained by the volumetric and by the quartz-crystal microbalance method show the same qualitative trends of the kinetics of the water vapour reaction for both systems discussed. In the volumetric experiments the high initial absorption rate with reaction probability of unity is much longer for O_2 than for H_2O. The gravimetric results indicate fast initial steps only in oxygen for both metals. The subsequent parallel exponential reduction of the reaction probability of r_{H_2O} and r_{O_2} in Figs. 3 and 4 is found again in the parallel course of the gravimetric curves in Figs. 1 and 2. The almost constant reaction probability of H_2O on iron films from about 8 ML N_{H_2O} in Fig. 3 corresponds to the upward bending of the semilogarithmic weight gain curve in Fig. 1. For both systems markedly enhanced hydrogen uptake from H_2O than from H_2 is indicated by the volumetric results.

Acknowledgments

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