ISSN 1330–0008
CODEN FIZAE4

INTERACTION OF OXYGEN AND WATER–VAPOUR WITH CLEAN AND HYDROGEN–PRECOVERED THIN IRON FILMS STUDIED BY SURFACE POTENTIAL MEASUREMENTS

WOJCIECH LISOWSKI and RYSZARD DUŚ

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Received 7 April 1995

Revised manuscript received 31 May 1995

UDC 538.971

PACS 68.45.Da

Oxygen adsorption on both clean and hydrogen–precovered thin Fe films has been investigated by measuring the surface potential (SP), gas phase composition and the total gas pressure at 298 K. The results were supplemented by SP studies of water-vapour adsorption on clean and oxygen-precovered thin iron films. Oxygen interaction with Fe film pre-exposed to water-vapour has also been studied at 298 K. It has been observed that only a small part of the initially deposited hydrogen desorbs due to the competitive adsorption of oxygen. Most of the hydrogen adspecies remain on the surface diminishing the amount of adsorbed oxygen and affecting the electrical character of the oxygen adsorbate. Water adsorbs dissociatively on clean Fe film at 298 K, decreasing the SP. Precovering Fe film with O_2 at 298 K prevents the decomposition of water. The amount of oxygen consumed is only slightly diminished by water preadsorbed on clean Fe film at 298 K.

1. Introduction

Surface potential (*SP*) measurement [1] is a well–known experimental technique extensively applied to study adsorption of oxygen [2-5], hydrogen [6-10] and water [11,12] on iron surfaces.

Various states of adsorbed oxygen have been derived from the *SP* changes [3-5]. The initial decrease of *SP* was attributed to the formation of a monolayer of chemisorbed oxygen atoms, whereas the subsequent increase of *SP* was due to penetration of oxygen adatoms below the surface image plane and formation of a precursor of an iron oxide. An electronegatively polarized deposit of hydrogen was obtained mainly due to hydrogen adsorption on polycrystalline iron surfaces [6,7,9,10] and on (111) and (100) iron single crystal planes [8]. Water was reported to adsorb dissociatively at 298 K [12-14], forming the electronegatively polarized surface hydroxyls [12].

Only small experimental effort has been devoted to investigate the interaction of hydrogen with oxygen on iron [2]. It is, therefore, the aim of this paper to study the adsorption of oxygen on hydrogen–precovered thin iron films. In order to provide further insight into this process, the adsorption of water vapour on both clean and oxygen–precovered thin Fe films as well as interaction of oxygen with water vapour–precovered Fe films have been investigated.

2. Experimental

The experiments were performed in glass UHV apparatus [15] capable of routinely reaching pressures of 1×10^{-10} Torr (Torr = 133.3 Pa). The ΔSP measurements were carried out applying a modified, rapidly recording static capacitor circuit [16]. The sensitivity was ±1 mV, the stability was 1 mV/h and the overall response time was 0.1 s. The static capacitor was made of Pyrex glass and consisted of two coaxial cylindrical electrodes [7]. The inner one, being the reference electrode, was coated with a conducting layer of ($SnO + Sb_2O_5$). This electrode was movable and could be moved up during thin Fe film deposition on the wall of the outer cylinder.

Iron films were deposited on Pyrex glass supports maintained at 78 K by evaporation of fine Fe wires (Johnson Matthey, grade I) wound around a tungsten heater, at pressures lower than 3×10^{-10} Torr. After evaporation, the films were sintered at 330 K for 30 min. The average geometrical area of the films was ≈ 160 cm^2, their average thickness was $\approx 10^{-5}$ cm and the roughness factor estimated by means of hydrogen adsorption [6] was $\approx 16 \pm 2$.

Spectroscopically pure oxygen and hydrogen (additionally purified by diffusion through a palladium thimble) were introduced in successive calibrated doses into the static capacitor kept at a constant temperature and disconnected from pumps by means of greaseless valves. The surface potential changes (ΔSP) were continuously recorded untill steady *SP* values were obtained after each dose. Pressure (P) was measured by means of a MacLeod manometer. Simultaneous recording of ΔSP and

P gives the relation of ΔSP versus oxygen (hydrogen) uptake (n), since the volume of the static capacitor was known.

Interaction of hydrogen–precovered Fe surfaces with O_2 was studied measuring ΔSP, gas phase composition (determined using a mass spectrometer–topatron, Leybold–Heraus) and total steady pressure P (MacLeod manometer), while oxygen was introduced into the system in successive calibrated doses.

The reaction of water vapour with Fe films was also investigated by monitoring the ΔSP. Water was degassed under HV conditions in a separate gas–handling part of the apparatus, by freeze–pump–thaw cycles repeated four–times. Then the water vapour was introduced into the static capacitor continuously through a connection with the water reservoir kept at 195 K (water-vapour pressure was 5.5×10^{-4} Torr [17]), without direct contact with the cold trap immersed in liquid nitrogen.

All adsorption experiments were performed at 298 K.

3. Results and discussion

3.1. Hydrogen adsorption on clean Fe *films*

The results concerning interaction of hydrogen with Fe films have been reported previously [6,7]. Three electronegatively polarized states of the adsorbate were detected at 298 K: (i) strongly bound β_s^-–adatoms, (ii) weakly bound β_w^-–atomic adspecies and (iii) molecular deposit α_E^-. In the experiments described below, hydrogen was preadsorbed on Fe film in successive doses at 298 K up to 10^{-1} Torr. The adsorption process was investigated by measuring ΔSP. Next, evacuation was performed to the final pressure approaching 10^{-7} Torr. In this way only strongly adsorbed, electronegatively polarized, hydrogen adspecies remained, covering about 60% of the Fe film surface. Oxygen was admitted in successive, calibrated doses into the static capacitor with such hydrogen-precovered Fe films.

3.2. Oxygen adsorption on clean and hydrogen–precovered Fe *films*

The values of ΔSP versus oxygen uptake n (called the surface potential isotherm) on both clean and hydrogen-precovered thin Fe film at 298 K are presented in Fig. 1. It is clearly seen that preadsorbed hydrogen affects the features of the ΔSP resulting from oxygen adsorption on Fe films. The negative SP transients (A in Fig. 1) appear up to $\theta \approx 2.4$. The negative transients recordered as a result of oxygen adsorption on clean Fe film at 298 K (C in Fig. 1) are observed up to $\theta \approx 6.4$ whereas the partial pressure of oxygen remains lower than 10^{-6} Torr (Fig. 1).

Analysis of the gas phase composition revealed that oxygen from the first successive doses introduced into static capacitor replaces hydrogen on the Fe surface removing H_2 into the gas phase. Oxygen pressure remains lower than 10^{-6} Torr. Assuming that the constant pressure (1.2×10^{-3} Torr) maintained after the introduction of several successive oxygen doses (Fig. 1) is the final pressure of hydrogen removed from the surface, one can calculate the number of desorbed H_2 molecules to be 1.8×10^{17}. This is only 16% of the hydrogen population evaluated during adsorption at 298 K. Most of the hydrogen adspecies remain on the Fe surface affecting the course of ΔSP during oxygen adsorption.

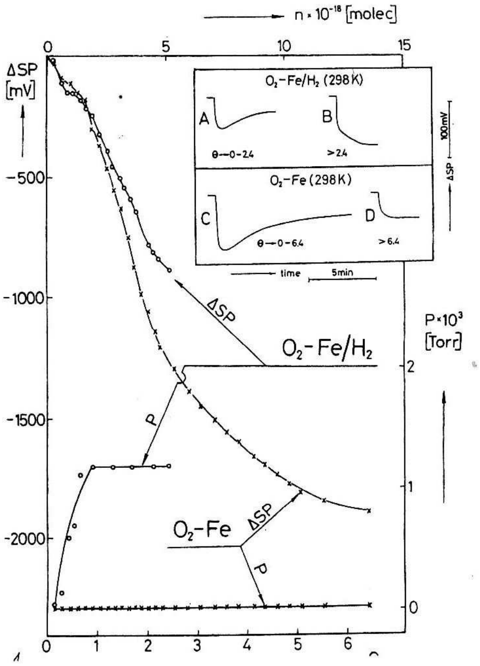


Fig. 1. Surface potential isotherms for O_2–Fe *and* O_2–Fe/H_2 *adsorption systems at 298* K. *Each dose of introduced oxygen contained:* 3.24×10^{17} *(*O_2–Fe*) and* 2.86×10^{17} *(*O_2–Fe/H_2*) molecules. The curves marked* P *show the dependence of the gas phase pressure on the population (and coverage) of oxygen admolecules.* ΔSP *features, for the distinguished steps of oxygen adsorption resulting from successive introduction of* O_2*, are shown in the inset.*

At O_2 pressure of the order of 10^{-2} Torr, a negatively polarized, weakly bound, molecular adsorbate is formed (B in Fig. 1). Similar form of oxygen adspecies was detected on clean Fe film (D in Fig. 1).

3.3. Water vapour adsorption on clean and oxygen-precovered Fe *films*

Fig. 2 shows the SP isotherms of water vapour adsorption on clean and oxygen–precovered thin Fe films at 298 K. Taking into account the water vapour pressure (5.5×10^{-4} Torr) and the time of exposition ($\approx$ 25 min (Fig. 2)) one can estimate the exposure of the Fe film to water to be $\approx 6 \times 10^5$ L. Such exposure produces an overlayer less than one layer thick of water adspecies [13].

Water was reported to adsorb dissociatively at 298 K forming surface hydroxyls [12-14]. Our *SP* measurements confirm significant decomposition of water adsorbed at ambient temperature, revealing a large decrease of *SP* at the beginning of adsorption, followed by an increase of *SP* after longer exposition (Fig. 2). Both adsorption of hydrogen and oxygen, as well as hydroxyl formation due to water decomposition, are expected to cause the *SP* decrease [12]. We suppose that decomposition of water to oxygen and hydrogen dominates at the beginning of adsorption. At higher coverage, H_2O decomposition to hydroxyl and hydrogen is more probable. However, in our experiments we observed a superposition of all the processes. After longer exposition, the adsorption of molecular water occurs, increasing the *SP* (Fig. 2).

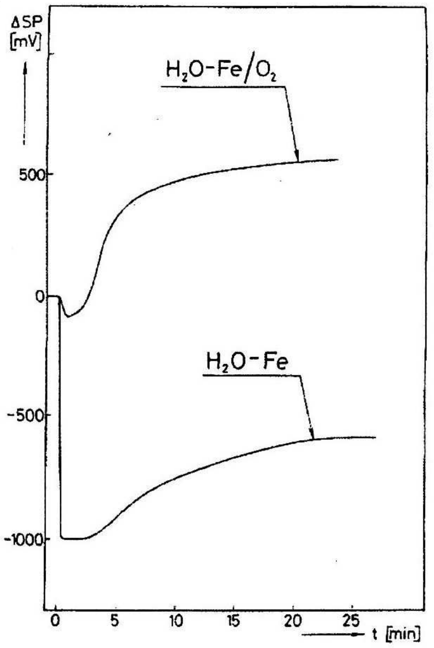


Fig. 2. The course of SP in the process of water vapour adsorption on clean and oxygen-precovered thin Fe *films at 298* K.

The preadsorbed oxygen prevents decomposition of water admolecules at 298 K, leading to an increase of *SP* (Fig. 2). A small decrease of *SP* at the beginning of adsorption, attributable to H_2O decomposition, can be caused by water adsorption on uncovered sites of the Fe film, arising due to incorporation of preadsorbed surface oxygen adatoms into the bulk of Fe film.

3.4. Oxygen adsorption on water vapour-precovered Fe *films*

The *SP* isotherm resulting from oxygen adsorption on Fe film precovered with water vapour at 298 K is shown in Fig. 3. Before O_2 adsorption, the Fe film was exposed to water vapour ($\approx 6 \times 10^5$ L) and then the system was evacuated until the pressure decreased to $\approx 10^{-7}$ Torr.

It can be seen that positive ΔSP (A in the inset to Fig. 3) at the beginning of adsorption resulted in the total ΔSP increasing up to $\theta \approx 0.2$ (Fig. 3). Then negative transients are observed. Strong transients, arising at the beginning of the process (B in the inset to Fig. 3), are followed by much less pronounced transients (C in the inset to Fig. 3) detected up to $\theta \approx 2.7$. Further O_2 doses cause only monotonic decrease of SP (D in the inset to Fig. 3).

Apart from the first step of adsorption ($\theta \leq 0.2$), the course of the SP isotherm seems to be similar to that recordered for oxygen adsorption on clean Fe film at 298 K (Fig. 1). However, in contrast to the clean Fe film, the adsorption of oxygen on water-precovered Fe film is accompanied by monotonic increase of the total pressure in the gas phase (Fig. 3). The analysis performed at the beginning of oxygen adsorption revealed hydrogen in the gas phase. Water, if adsorbed, was selectively removed by the traps cooled in liquid nitrogen.

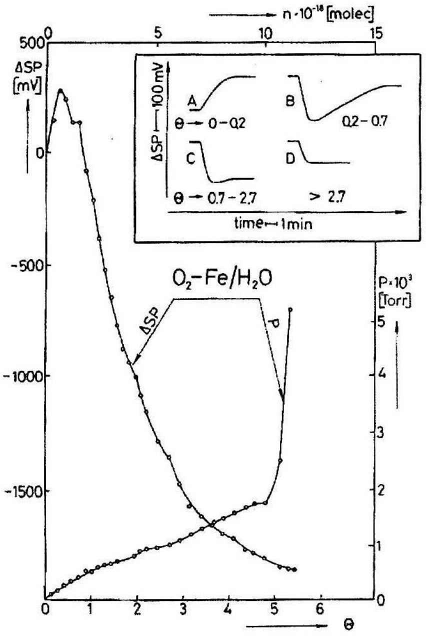
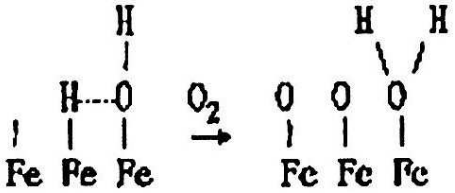


Fig. 3. Surface potential isotherm for O_2–Fe/H_2O *adsorption system at 298* K. *Each dose of introduced oxygen contained* 3.13×10^{17} *molecules. The curve marked* P *shows the dependence of the gas phase pressure on the population (and coverage) of oxygen admolecules.* ΔSP *features, for the distinguished steps of oxygen adsorption resulting from successive introduction of* O_2*, are shown in the inset.*

The course of the SP isotherm resulting from oxygen adsorption on water–precovered thin Fe film (Fig. 3) indicated a large oxygen sorption, only slightly smaller than that found for the O_2–Fe system (Fig.1). The increase of SP at the beginning of adsorption can be caused by: (i) competitive desorption of hydrogen and (ii) reassociation of H_2O admolecules due to O_2 interaction with the products of preadsorbed water decomposition. The latter process can be modelled as follows:



These two processes can overlap. The observed, relatively high increase of SP, accompanied by rather low pressure of the gas phase (Fig. 3) suggest the importance of the second assumption.

4. Conclusions

(1) Interaction of oxygen with hydrogen–precovered thin Fe film leads to adsorption of oxygen at 298 K. A small amount of hydrogen adsorbate is removed due to competitive adsorption of oxygen. A significant amount of hydrogen adspecies remains on the surface, affecting the course of ΔSP accompanying oxygen adsorption. No evidence has been found for hydroxyl formation due to oxygen interaction with hydrogen adatoms precovering thin Fe film at 298 K.

(2) Water adsorbs dissociatively on thin Fe film at 298 K, decreasing SP. The oxygen preadsorbed at 298 K prevents decomposition of water adsorbing with the increase of SP. Hence the surface potential measurement can be an useful method for detection of oxide layer defects on Fe film surfaces.

(3) Preadsorbed water affects the course of SP accompanying oxygen adsorption at 298 K, but the amount of oxygen adsorbed is only slightly smaller than that found for the O_2–Fe system.

References

1) F. C. Tompkins, *Chemisorption of Gases on Metals*, (Academic Press, London, 1978).

2) C. M. Quinn and M. W. Roberts, Trans. Faraday Soc. **60** (1964) 899;

3) G. K. Hall and C. H. B. Mee, Surf. Sci. **28** (1971) 598;

4) G. Alshorachi and G. Wedler, Appl. Surf. Sci. **20** (1985) 279;

5) C. F. Brucker and T. N. Rhodin, Surf. Sci. **57** (1976) 523;

6) E. Nowicka, W. Lisowski and R. Duś, Surf. Sci. **137** (1984) L85;

7) E. Nowicka and R. Duś, Surf. Sci. **144** (1984) 665;
8) F. Bozso, G. Ertl, M. Grunze and M. Weiss, Appl. Surf. Sci. **1** (1977) 103;
9) R. Culver, J. Pritchard and F. C. Tompkins, Z. Electrochem. Ber. Bunsenges. Physik. Chem. **63** (1959) 741;
10) R. Suhrmann, A. Hermann and G. Wedler, Z. Physik. Chem. (Frankfurt am Main) **35** (1962) 155;
11) J. M. Heras and E. V. Albano, Appl. Surf. Sci. **17** (1983) 207;
12) P. A. Thiel and T. E. Madey, Surf. Sci. Rep. **7** (1987) 211;
13) J. K. Gimzewski, B. D. Padalia, S. Affrossman, L. M. Watson and D. J. Fabian, Surf. Sci. **62** (1977) 386;
14) M. W. Roberts and P. R. Wood, J. Electr. Spectr. Relat. Phenom. **11** (1977) 431;
15) W. Lisowski, Surf. Sci. **312** (1994) 157;
16) T. Delchar, A. Eberhagen and F. C. Tompkins, J. Sci. Instr. **40** (1963) 105;
17) A. Wexler, J. Res. Natl. Bur. Std. (US) **81A** (1977) 5.

PROUČAVANJE UZAJAMNOG DJELOVANJE KISIKA I VODENE PARE SA ČISTIM I VODIKOM PREKRIVENIM TANKIM SLOJEVIMA ŽELJEZA MJERENJEM POVRŠINSKIH POTENCIJALA

Proučavana je adsorpcija kisika na čistim i vodikom prekrivenim tankim slojevima željeza mjerenjem površinskog potencijala, sastava plina i ukupnog tlaka na 298 K, kao i adsorpcija vodene pare na čistim i kisikom prekrivenim tankim slojevima željeza. Proučavano je, također, međudjelovanje kisika s Fe slojem prethodno izloženom vodenoj pari. Prekrivanje Fe sloja s kisikom na 298 K spriječava dekompoziciju vode. Količina potrošenog kisika samo se malo smanjuje preadsorbiranom vodom na čistom Fe sloju na 298 K.