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Reduction by Hydrogen of Oxidized Surfaces of Fe(100) and Pt-Covered Fe(100)

G. W. R. LEIBBRANDT[1] AND F. H. P. M. HABRAKEN

Department of Atomic and Interface Physics, Debye Institute, University of Utrecht, P.O. Box 80,000, 3508 TA Utrecht, The Netherlands

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The reduction at 555 K of oxidized Pt/Fe(100) surfaces by H_2 has been studied using ellipsometry and Auger electron spectroscopy in combination with Ar^+ ion bombardment. The surfaces considered here were first covered with Pt (0–1.1 monolayer) and then oxidized up to different oxygen uptakes. It is found that the initial rate at which the oxygen is removed by the hydrogen strongly decreases with oxide thickness and with initial Pt coverage. If the oxygen uptake exceeds 7×10^{15} atoms/cm^2, the surfaces cannot be reduced. After deposition of about 0.5 monolayer Pt on top of such an oxide layer, exposure to H_2 results in a reduction at the same rate as for thin oxide layers. It is concluded that the oxide can only be reduced if metallic atoms are available at the surface.

1. INTRODUCTION

From a catalysis point of view, there is a large interest in the understanding of the reduction by hydrogen of oxidized Fe surfaces and surfaces of materials that contain iron. Iron serves as an important catalyst in the hydrogenation of CO (*1*) and in ammonia synthesis (*2*). In addition, there is a catalytic interest in bimetallic systems containing Fe and a more noble Group VIII metal like Rh, Pd, or Pt (*3*). It has been reported recently that the rate of selective hydrogenation of the aldehyde group in cinnamaldehyde and crotonaldehyde in the presence of $Pt_{1-x}Fe_x$ has a strong and narrow maximum around $x = 0.2$ (*4, 5*). In all these instances the activity of the catalyst is greatly determined by the extent to which the iron is in its reduced state. Vink *et al.* (*6*) have studied the reduction by hydrogen of oxidized Fe(100) surfaces. They found that H_2 gas pressures of about 1 Pa are necessary to obtain a significant reduction rate. The hydrogen reacts with oxygen at the surface and there is a continuous supply of oxygen to the surface of the oxide. The reduction rate is about 50 times higher at 650 K than at 475 K. At all temperatures, there is a residual amount of oxygen which cannot be removed from the surface. Vink *et al.* estimate this amount to be one monolayer. In the reduction of the oxidized Fe(110) surface this effect is not observed: all oxygen can be removed by hydrogen (*7*).

Recently, Vreeburg *et al.* (*8*) have shown that no oxygen is removed from a fully oxidized Fe monolayer deposited on a Ni(111) surface if it is exposed to H_2 in the fashion described above. They argue that this difference with the reduction of an oxidized surface of bulk Fe is caused by a difference in stoichiometry of the oxide. We have determined previously that the average stoichiometry of the oxide which forms on Fe(100) at room temperature and 475 K is $Fe_{0.95\pm0.05}O$ (*9*). The Fe content of the iron oxide layer on the Ni(111) surface might be lower (Fe_2O_3, Fe_3O_4).

We have recently reported extensively on the growth of oxides on the Fe(100) surface, at different temperatures and precovered with varying amounts of Pt (*10–12*). We have represented some typical results as a brief summary in Fig. 1. It was found that, after an initial fast stage, the oxide

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[1] Present address: Philips Research Laboratories, Eindhoven, The Netherlands.

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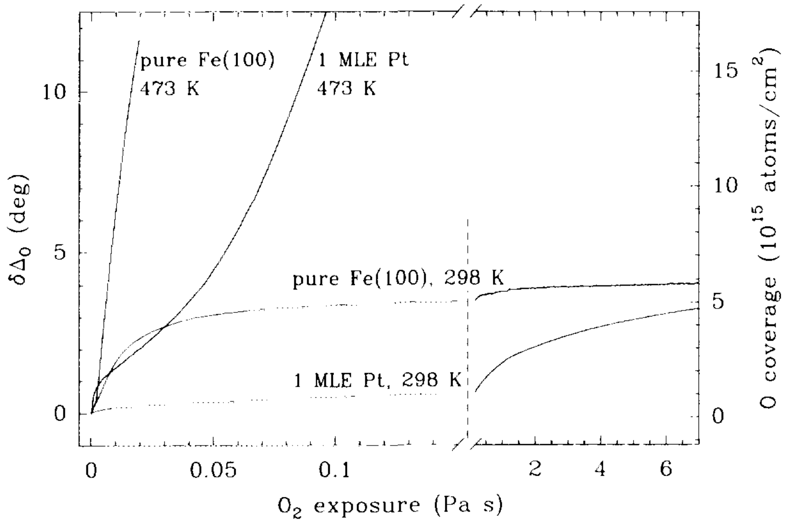

FIG. 1. Typical ellipsometry data for the oxidation of Fe(100), with and without Pt coverage and at different temperatures. The continuation of the oxidation curves at room temperature and high exposures has been included in the right-hand part of the figure.

growth process at room temperature on the pure Fe(100) surface virtually stops after an oxygen uptake of about 6×10^{15} atoms/cm^2. This corresponds to an oxide thickness of about 1 nm. Above 425 K no such saturation is observed, and much thicker oxide layers can be grown. It was also demonstrated that the process of oxide growth proceeds by the transport of cations (Fe ions) from the metal substrate through the oxide layer. We have argued (*12*) that these phenomena can be understood within the framework of the theory of metal oxidation of Fromhold and Cook (*13*). This theory states that either the supply of reactants (Fe from the bulk, O from the gas phase) or the supply of electrons determines the oxidation rate. Initially, reactant supply is always rate limiting. As the oxide layer thickens, electron transport becomes increasingly difficult. At low temperatures (viz., <425 K) electron transport proceeds by tunneling. As the tunnel current is an exponential function of thickness, this current drops to zero above a certain thickness, and the oxide growth virtually stops. At more elevated temperatures electron transport can proceed by thermionic emission of electrons from the metal into the conduction band of the oxide, and oxide growth continues to proceed.

Pt grows in a layer-by-layer fashion on Fe(100) (*14*). Pt depositions in submonolayer and monolayer amounts have a moderating effect on the oxidation of the Fe(100) surface. This is expected since the oxygen reactivity of Pt is much lower than that of Fe. It appears, however, that the presence of several monolayers of Pt does not inhibit the formation of oxide layers. After oxidation no Pt is present at the surface, but is found at the oxide/metal interface.

In this paper we investigate the reduction by H_2 gas of Fe(100) and Pt/Fe(100) surfaces which were oxidized under different conditions. The sample temperature was kept at a fixed value and had to be chosen with some consideration. On the one hand, it should not be chosen too low, in order for the reduction process to proceed at all. On the other hand, it was shown previously (*14*) that above 575 K Pt forms a $Pt_{0.5}Fe_{0.5}$ alloy with the Fe substrate, which introduces extra complications. All H_2 exposures were therefore performed at a sample temperature of 555 K.

In the following the Pt and O coverages will often be expressed in monolayer equivalents (MLE). Here, 1 MLE equals the number of Fe atoms in a {100} layers: 1.22 × 10^{15} atoms/cm^2.

2. EXPERIMENTAL

The experiments have been performed in OCTOPUS. This is a surface analysis system consisting of a load lock and three interconnected UHV chambers. One of these serves as a scattering chamber at the end of the Utrecht University 3 MeV Van de Graaff accelerator, used to perform Rutherford backscattering spectrometry, high energy ion scattering with shadowing and blocking, and nuclear reaction analysis. In addition, the system contains facilities for LEED (low-energy electron diffraction), AES (Auger electron spectroscopy), ellipsometry, Pt evaporation, low-energy ion sputtering, and annealing. The base pressure is in the low 10^{-8} Pa region. Oxygen pressures are measured using an electrostatic quadrupole mass spectrometer.

The process of adsorption and removal of oxygen at the surface was studied using ellipsometry. In ellipsometry measurements, circularly polarized light is directed, off normal, at the surface under consideration. Upon reflection, the phase-shift and change in amplitude will in general not be the same for the parallel and the orthogonal component of the light. As a result, the reflected light will be elliptically polarized, rather than circularly. Shifts in phase and attenuation are determined by the optical components of the reflecting layers. Analysis of the polarization state yields two parameters, denoted as Δ and ψ, which carry information about the reflecting surface.

Our ellipsometer is arranged in the polarizer-comparator-surface-analyzer (PCSA) configuration (*15*). The rotations of the polarizer and the analyzer are driven by means of computer controlled stepping motors. The measurements are performed at a wavelength of 554 nm and with an angle of incidence of 70° with the surface normal. Continuous measurements during gas exposures are performed by measuring the decrease of Δ relative to the value of Δ at the onset of the experiment. These values are checked with independent null-measurements before and after the gas exposure.

In Ref. (*12*) it is demonstrated, using high-energy ion scattering techniques, that the decrease of the ellipsometric parameter Δ ($\delta\Delta$) is a direct and linear measure of the amount of oxygen taken up by the Fe(100) surface, after an initial chemisorption stage, for which the technique is insensitive. The offset due to this chemisorption is 0.25 × 10^{15} O atoms/cm^2. The linear correspondence holds at least up to $\delta\Delta_O = 20°$ or 28 × 10^{15} O atoms/cm^2 and is the same for both pure and Pt-covered Fe surfaces.

Platinum deposition was done using a Pt evaporator described in Ref. (*16*). Pt coverages were determined in Rutherford backscattering spectrometry measurements. Sputter profiles in combination with AES were measured by bombarding the surface with 600-eV Ar^+ ions at 70° off normal incidence. The ion flux was 2 μA/cm^2. The primary electron energy for AES was 1500 eV.

The standard cleaning procedure of the Fe(100) surface consisted of sputtering (1000 eV Ar^+) for 30 min at 550 K and subsequently 15 to 30 min at 700 K, followed by 7–10 min anneal at 700 K. This procedure resulted in a clean surface, covered with less than 5% of a monolayer of contaminants (mainly C and N) as indicated by AES and with a sharp (1 × 1) LEED pattern.

3. RESULTS

In a series of experiments various amounts of Pt were evaporated onto an Fe(100) surface which was kept at room temperature. Without further treatment, these surfaces were subsequently exposed at room temperature to O_2 gas at a pressure between 10^{-4} and 10^{-3} Pa. The oxidation

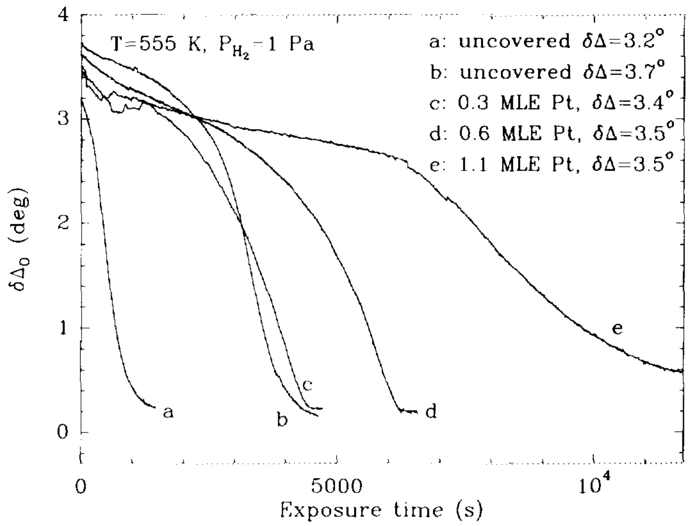

FIG. 2. δΔ versus H_2 exposure for two pure Fe(100) surfaces oxidized up to different oxygen uptakes, and oxidized Fe(100) precovered with 0.3 MLE Pt, 0.6 MLE Pt, and 1.1 MLE Pt, respectively.

process was followed in situ using ellipsometry. The O_2 gas supply was stopped in all cases when the ellipsometric parameter $\delta\Delta_O$ had reached a value of 3.4°. From the calibration described in Ref. (*12*), it follows that this corresponds to an oxygen uptake by the surface of 4.9×10^{15} O atoms/cm^2. In addition, in two experiments, the Fe(100) surfaces were exposed to O_2 up to $\delta\Delta_O = 3.2°$ and $\delta\Delta_O = 3.7°$, corresponding to oxygen uptakes of 4.6×10^{15} O atoms/cm^2 and 5.3×10^{15} O atoms/cm^2, respectively. The relative accuracy in the determination of oxygen uptake in these experiments is less than 0.1° in $\delta\Delta_O$ or about 0.1×10^{15} O atoms/cm^2.

The surfaces prepared in the fashion described above were subsequently exposed to H_2 at a pressure of 1 Pa and at a sample temperature of 555 K. During the H_2 exposure the surfaces were continuously monitored using ellipsometry. The resulting reduction curves are given in Fig. 2. The starting level of the curves on the $\delta\Delta_O$ axis is the level reached in the preceding room temperature oxidation treatment, and $\delta\Delta_O = 0.0°$ is associated with a clean surface. A decrease of the $\delta\Delta_O$ value indicates that the amount of oxygen, incorporated in the surface, decreases. From Fig. 2 it is clear that oxygen is removed from the surface as a result of H_2 exposure. On the pure iron surface, it appears that the rate at which the reduction proceeds is strongly dependent on the initial oxygen uptake. The reduction of the surface which was oxidized up to $\delta\Delta_O = 3.7°$ starts at a much lower rate than that on the surface oxidized up to $\delta\Delta_O = 3.2°$. After an initial slow part, however, the rate of the process increases and the reduction reaches a second stage in which the oxygen removal proceeds linearly with exposure at a practically equal rate compared to the less oxidized surface. The same initial slow part is observed on the Fe(100) onto which Pt was deposited before oxidation. The duration of this first stage increases with increasing Pt coverage. In all cases, the decrease of $\delta\Delta_O$ stops around a value of $\delta\Delta_O \approx 0.2°$. Even after prolonged exposure of H_2 no further decrease is observed. AES measurements also indicate the presence of oxygen at the surface in an amount of several tenths of a monolayer. Therefore we conclude that not all oxygen can be removed from the surface. For the pure surface this is in agreement with Vink *et al.* (*6*) who have found that H_2 treatment at temperatures in the range of 500–650 K of oxidized Fe(100) is not capable of removing a residual amount of oxygen from the surface. Their ellipsometry signal also indicates a value of $\delta\Delta_O = 0.2°$ for this residual amount. From the relation between $\delta\Delta_O$ and oxygen uptake (*12*) it follows that $\delta\Delta_O = 0.2° \pm 0.1°$ corresponds to an oxygen coverage of $(0.5 \pm 0.2) \times 10^{15}$ O atoms/cm^2, i.e., (0.4 ± 0.2) MLE. The ability to reproduce this result in two different places is a strong indication that this effect is not caused by traces of impurities in the H_2 gas.

As was mentioned in the Introduction, after room temperature oxidation of an Fe(100) surface onto which Pt has been deposited in the (sub)monolayer coverage range, the Pt atoms are located at the oxide–metal interface (*10, 11*), as was concluded on the basis of AES-sputter profiles. In the same fashion we have studied the Pt-covered Fe(100) surfaces after oxidation and subsequent reduction by H_2. Figure 3 shows a typical result. Immediately after reduction of the surface virtually no Pt is visible with AES. This indicates that no Pt is present in the immediate surface region. The thickness can be estimated from the fact that the magnitude of the Pt 237-eV signal (Pt_{237}) signal before sputtering is about 10–15% of its maximum value. This indicates that the Pt is located at the depth which roughly equals about twice the attenuation length of 237-eV electrons. We have determined previously, using the same experimental parameters, that this value is $(4.3 \pm 0.3) \times 10^{15}$ atoms/cm^2 in Pt. There may be some element dependence in this attenuation length, resulting in a larger value in an Fe layer, but the differences are known to be small (*17*). Correcting for the fact that Auger electrons are detected at an angle of 42.3° off normal, this means that the Pt atoms are located underneath about 6×10^{15} atoms/cm^2. This is roughly the same number of Fe atoms as were consumed in the formation of the oxide layer. The Pt profile curve therefore shows that the Pt is still located in a buried layer under-

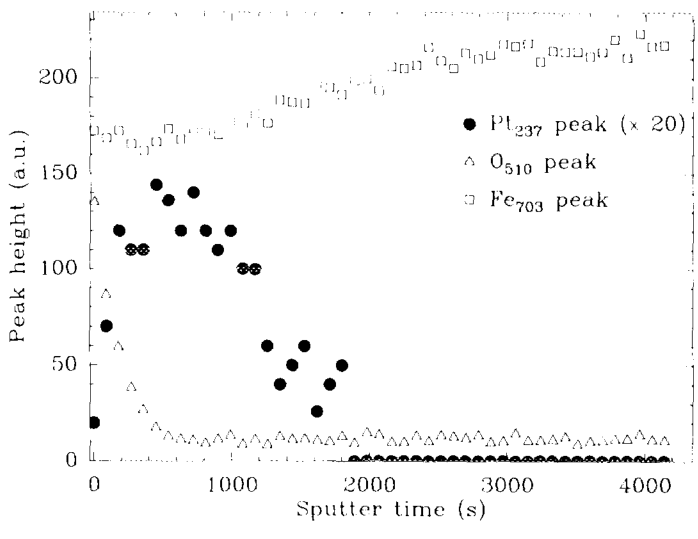

FIG. 3. The AES peak heights of the Pt_{237}, O_{510}, and the Fe_{703} peaks as a function of sputter time of the Fe(100) sample which was covered with 1.1 MLE Pt, subsequently oxidized at room temperature up to an oxygen uptake of 4.9×10^{15} O atoms/cm^2, and finally reduced in H_2 at a temperature of 555 K.

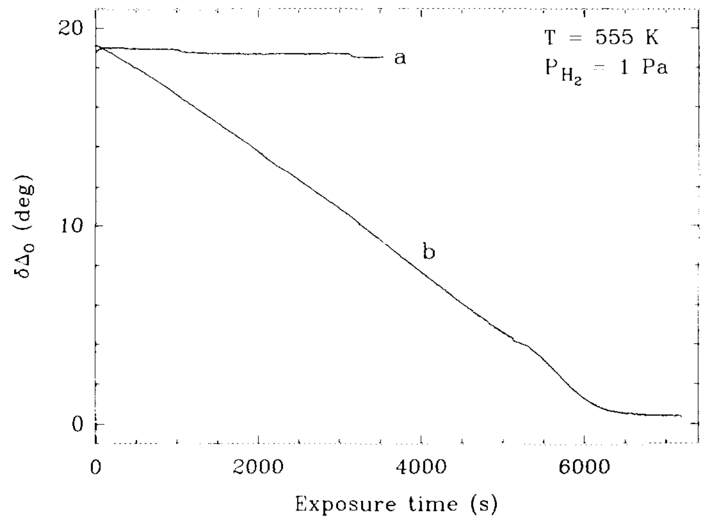

FIG. 4. $\delta\Delta_O$ as a function of H_2 exposure for an Fe(100) surface, covered with 1 MLE Pt and subsequently exposed up to an oxygen uptake of 26.6×10^{15} O atoms/cm^2 (a) and for a similarly prepared sample onto which, after oxidation, an additional 0.5 MLE Pt was evaporated (b).

neath a now-reduced Fe surface layer. The nonzero value of the O_{510} peak height at the onset of sputtering reflects the incapability of H_2 exposure to remove the last half oxygen monolayer, which effect was discussed above.

We noted above that the initial reduction rate is strongly dependent on the amount of oxygen taken up by the Fe(100) surface in the preceding oxidation step. By performing the oxidation step at higher temperatures, much higher oxygen uptakes can be achieved on both pure and Pt covered Fe(100) surfaces (*11*). We found that above oxygen uptakes of about 7×10^{15} O atoms/cm^2 ($\delta\Delta_O = 5°$), no removal of oxygen could be measured using ellipsometry during H_2 exposures of more than 1 h ($\sim 10^4$ Pa · s) on both pure and Pt-covered Fe(100) surfaces.

H_2 dissociates very easily on Pt surfaces. However, the presence of Pt on the surface before the oxidation does not result in an increase in the reduction rate. This is consistent with the observation that after oxidation of a Pt-covered Fe(100) surface Pt is found at the metal/oxide interface instead. In order to check whether the presence of Pt at the surface can indeed enhance the reduction process we performed the following experiment. One MLE Pt was evaporated onto an Fe(100) surface that was subsequently oxidized up to 26.6×10^{15} O atoms/cm^2 at a temperature of 475 K. Upon exposure to H_2 at 555 K no change in $\delta\Delta_O$ was observed, as is indicated by curve a in Fig. 4. Subsequently, the surface was cleaned and again prepared in the same way. Before exposing this surface to H_2, approximately 0.5 MLE Pt was evaporated on the surface. Curve (b) in Fig. 4 shows the resulting development of $\delta\Delta_O$ with H_2 exposure. $\delta\Delta_O$ decreases linearly with exposure with the same rate as was observed in the second stage in the $\delta\Delta_O$ vs H_2 exposure curves of Fig. 2.

4. DISCUSSION

4.1. Availability of Metallic Atoms at the Surface

From the measurements given in Fig. 4, we conclude that the availability of metallic atoms at the surface is crucial for the reduction of the oxide layer on the Fe(100) and the Pt/Fe(100) surface. The metallic atoms most probably serve as dissociation sites for H_2. Once these sites are available, the removal of oxygen proceeds at a rate that is constant for the fixed temperature and H_2 pressure that we used in these experiments. By reduction of the iron oxide layer, metallic iron will become available to serve as dissociation centers. In this fashion the number of dissociation sites increases. It is therefore conceivable that each reduction process eventually reaches the constant rate of oxygen removal, such as that given in Fig. 2.

Figure 2 shows that with increasing amounts of Pt, present at the surface before oxidation, the initial reduction rate decreases. It was also shown that with increasing thickness of the oxide layer this initial reduction rate decreases. This indicates that in both cases the availability of metallic atoms at the surface decreases.

In contrast to the phenomena observed by Vreeburg *et al.* (*8*) discussed in the Introduction, these observations are difficult to explain by a difference in stoichiometry between the surfaces that are easily reduced and the ones that are not. We have demonstrated elsewhere (*11, 12*) that the average stoichiometry is equal for all oxides considered in this study.

The above therefore implies that on oxidized iron surfaces metallic (neutral) iron atoms are present at the oxide surface. One may consider the possibility that there is some diffusion of neutral iron atoms from the Fe bulk through the oxide layer to the surface, and that consequently there is a nonzero amount of neutral Fe atoms on the surface. Following this assumption, the observed dependence of the initial reduction implies that the rate of this diffusion becomes lower with increasing oxide thickness, or with increasing amounts of Pt at the interface. However, if an oxide is in thermodynamic equilibrium with the substrate at a temperature at which such atoms are mobile, the dissolved atoms are supposed to dissociate into (interstitial) cations and electrons (*18*). It is therefore unlikely that a neutral atom will reach the oxide surface by diffusion from the bulk. Alternatively, a metallic iron atom at the oxide surface can be conceived as a surplus cation which is (temporarily) neutralized by a surplus electron. As was pointed out in the Introduction, cation and electron transport during oxidation are described by the theory of metal oxidation of Fromhold and Cook (*13*).

4.2. Cation and Electron Transport

We will consider on a speculative basis whether some concepts of the Fromhold–Cook theory can also be applied to the reduction process. In this theory, cation (Fe^+, Fe^{2+}) transport across the oxide layer is assumed to be fairly easy, and there will be an equilibrium amount of cations at the surface. Fromhold and Cook estimate the ratio between cation concentration at the metal-oxide interface and the oxide surface to be 10^3. If we assume the cation concentration at the metal-oxide interface to be 10^{16} atoms/cm^2, it follows that the equilibrium concentration at the surface is 10^{13} cations/cm^2, or roughly 0.01 MLE. According to Fromhold and Cook, electron transport is rate-limiting in the oxidation process for oxide layers on Fe(100) exceeding approximately 1 nm. The situation for electron transport can be described in a similar electron energy diagram as during oxidation, where the level in oxygen is now replaced by a level in iron.

Figure 1 indicates that at temperatures around 555 K the oxidation proceeds at a considerable rate on Fe(100) surfaces on which Pt and/or oxide is present in amounts for which we presently find that the reduction is effectively inhibited. This seems inconsistent with the idea of the same rate limiting step for oxidation and reduction. There are two differences between the situation during oxidation and during reduction. One is the difference in the electron energy level scheme at the oxide-gas interface mentioned above. The other is that the equilibrium amount of cations at the surface, which now serve as electron trapping centers, is probably much smaller than the amount of adsorbed oxygen atoms which serve as electron trapping centers during the oxidation. It remains, however, unclear whether this can sufficiently explain the observed difference in oxidation rate and reduction rate. We have discussed previously that the rate of electron transport decreases with both increasing oxide layer thickness and with increasing Pt present at the oxide–metal interface. This again is consistent with our present observations. We therefore cautiously conclude that phenomena observed in the reduction of oxide layers on Fe(100) and Pt/Fe(100) can be understood qualitatively in the framework of the Fromhold–Cook theory of metal oxidation.

The above may also offer an alternative explanation for the fact that a thin iron oxide layer on a Ni(111) substrate cannot be reduced by H_2, as observed by Vreeburg *et al.* (*8*). In this case, there is no iron substrate which can supply cations to diffuse to the surface, since all available Fe atoms are incorporated in the oxide. This argument requires the assumption that nickel atoms from the substrate cannot diffuse as cations through the oxide in a similar fashion as iron atoms.

5. CONCLUSIONS

We have shown that Fe(100) and Pt/Fe(100) surfaces upon which an oxide layer with an oxygen content of up to 5–6 × 10^{15} atoms/cm^2 was grown can be reduced in H_2 at a temperature of 555 K. The reduction rate at the onset of H_2 exposure decreases with increasing oxide thickness and with increasing amounts of Pt deposited before oxidation. After this initial stage the reduction proceeds at the same constant rate for all Pt coverages and all considered extents of oxidation. At 555 K, the Pt/Fe layer structure is stable. Above 575 K alloying takes place and other phenomena may occur which are beyond the scope of this work and these conclusions.

It was found previously that after oxidation of an Fe(100) surface onto which Pt was evaporated, the platinum atoms are located at the oxide–metal interface. After reduction of such a surface, the platinum atoms are buried underneath a pure Fe layer.

If the oxygen uptake exceeds roughly 7 × 10^{15} atoms/cm^2, no oxygen can be removed from the surface by H_2 exposure. After deposition of about 0.5 MLE Pt on top of such an oxide layer, the reduction proceeds at a constant rate directly from the onset of the H_2 exposure. This suggests that reduction by H_2 of iron oxide can only proceed if metallic atoms are present at the surface. We conclude that the way the reduction proceeds initially is related to the concentration of metallic atoms at the surface of the oxide.

The variation of the oxygen removal rate at the onset of H_2 exposure can qualitatively be understood within the framework of the theory of metal oxidation of Fromhold and Cook (*13*).

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