

## THE INTERACTION OF HYDROGEN AND CARBON MONOXIDE WITH OXYGEN ON Cu(110)–Fe SURFACES

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The interaction of hydrogen and carbon monoxide with oxygen adsorbed on Cu(110)–Fe surfaces has been studied with ellipsometry, Auger electron spectroscopy and low energy electron diffraction. With carbon monoxide copper can be reduced completely and  $\text{Fe}_{0.95}\text{O}$  partially. With a model which is only an extension of the scheme for the reduction of pure Cu(110) by CO, the reduction of Cu(110)–Fe can be simulated. The lateral orientation of  $\text{Fe}_{0.95}\text{O}$  with respect to the copper matrix changes during repetitive oxidation–reduction cycles. At 725 K oxygen deficient iron oxide segregates to the surface. With hydrogen all oxygen can be removed.

### 1. Introduction

In this paper investigations on the reaction of carbon monoxide and hydrogen with oxygen adsorbed on Cu(110)–Fe surfaces are described. The surface alloys are prepared by thermal decomposition of iron carbonyl onto a clean Cu(110) surface [1].

Carbon monoxide reacts readily with oxygen adsorbed on copper surfaces even when it is alloyed with iron. On Cu(111)–Fe it was observed that CO did not react with iron oxide (except in the case of  $\gamma\text{-Fe}_2\text{O}_3$ ). This parallels the behaviour on pure iron [3], but oxygen adsorbed on bare copper could be removed easily.

The dependence of the reaction rate of hydrogen with oxygen on the hydrogen pressure is  $p^{1.0}$  for pure Cu(111) but changes to  $p^{0.5}$  when Cu(111) is alloyed with iron [2] even at small amounts of iron [4]. The reaction rate of the main reduction stage was proportional to the amount of iron deposited.

The purpose of this study is to investigate whether Cu(110)–Fe has the same properties as Cu(111)–Fe or, if other features are observed, try to explain the differences in terms of geometrical arguments.

### 2. Experimental

For the technical data, the crystal preparation and the calculation of the iron mole fraction we refer to refs. [1,5,6]. To determine a possible stoichiome-

try of iron the peak ratio  $h_O/h_{Fe}$ , where  $h_O = h_{515}$  is the peak to peak height of the oxygen AES 515 eV signal and  $h_{Fe} = h_{651}$ , was monitored during sputtering. Since copper could be reduced completely by CO, a constant peak ratio indicates a constant oxygen to iron ratio. The surface was sputtered with  $Ar^+$  ions of 450 eV at a current of  $500 \text{ nA cm}^{-2}$ . Based on the measurements performed on Cu(111)–Fe during 1000 s sputtering 6 atomic layers will be removed.

The interaction of  $H_2$  or CO with oxidized Cu(110)–Fe alloys was monitored continuously with ellipsometry. Since after oxidation no facets of iron are present [6] the parameter  $\delta\Delta$  can be taken directly proportional to the amount of oxygen. The absolute coverage of oxygen  $\theta_O$  is based on the occurrence of a  $(2 \times 1)$  LEED pattern on Cu(110) which is equivalent to  $\theta_O = 0.5$  [4,7].

### 3. Results

#### 3.1. Interaction with CO

The reaction of CO with fully oxidized Cu(110)–Fe surface alloys containing different amounts of iron is studied at pressures from  $10^{-3}$  to  $10^{-1}$  Pa and crystal temperatures of 475–750 K. The oxidation of a Cu(110)–Fe crystal was carried out in three or four steps. First the crystal was exposed to oxygen at 425 K until (almost) saturation occurred and subsequently the routine was repeated at 550 and 675 K; if CO was exposed above 675 K another oxygen exposure at 775 K was performed. When no such proper pretreatment was given relatively low reaction rates were measured especially at high temperatures and no straight Arrhenius plot was found. The experiments could only be performed at one iron mole fraction:  $x_H(Fe) = 0.20$  due to surface segregation effects [6].

As for Cu(111)–Fe it is impossible to remove all oxygen from the surface with CO in the pressure and temperature range studied. After CO exposures Auger spectra showed no carbon peak. The reaction rate is proportional to the CO pressure. At temperatures below 550 K the mole fraction of iron in the surface region,  $x_H(Fe) = 0.20$  does not change during CO exposure. At temperatures of 650–750 K  $x_H(Fe)$  increases to  $0.28 \pm 0.02$ ; at 550–650 K intermediate mole fractions are observed.

A significant difference in kinetics of oxygen removal and LEED patterns between the first CO exposure and those after the third CO exposure was observed. Therefore a distinction between those two reaction types is made.

##### 3.1.1. First admittance of CO

Fig. 1 shows  $\delta\Delta$  as a function of the CO exposure at different temperatures. First the reaction rate is slow, but then it abruptly increases and next falls

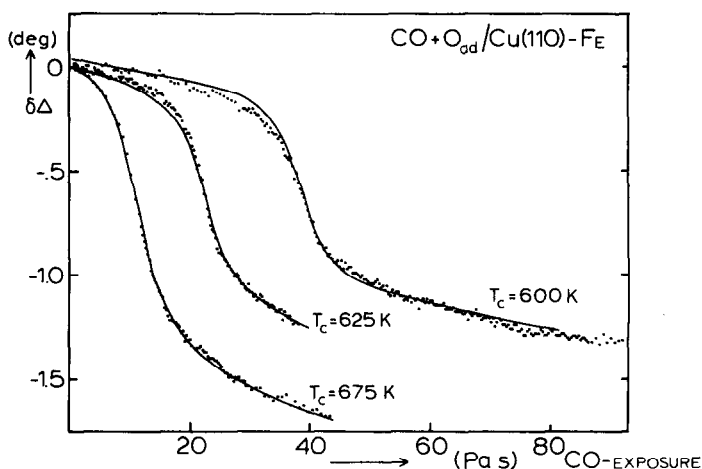


Fig. 1.  $\delta\Delta$  versus first CO-exposure to fully oxidized Cu(110)–Fe surface alloys at  $x_H(\text{Fe}) = 0.20$  and different temperatures. Solid lines denote solution of eqs. (2)–(5), (7) and (8).  $\delta\Delta = 0.5$  corresponds to  $\theta_O = 0.5$ .

gradually to zero. The first two stages are also observed on pure Cu(110) [4], although the second involves only a change of  $0.4^\circ$  in  $\delta\Delta$  there. So the total amount of oxygen which can be removed by CO is much larger than for pure Cu(110). The reaction probability of the fast reduction stage, defined as the number of oxygen atoms removed per incident CO molecule, was calculated as a function of  $1/T$  and is shown in fig. 2. The reaction rate on Cu(110)–Fe is 0.75 times the one on Cu(110). The apparent activation energies for Cu(110)–Fe and pure Cu(110) which can be deduced from this Arrhenius plot are equal within experimental error and are determined to be  $E_{\text{act}} = 31.5 \pm 0.5$  kJ/mol. Habraken and Bootsma [7] have measured  $E_{\text{act}} = 27 \pm 2$  kJ/mol for pure Cu(110) and an absolute reaction rate which is a factor 1.3 larger. The linear stage before the inflection point is analysed analogously. Above 550 K the apparent activation energy is  $E_{\text{act}} = 31 \pm 3$  kJ/mol, the absolute reaction rate depends on the temperature at which the final oxidation was performed and on the amount of iron deposited.

The AES peak ratio after prolonged reduction, only performed at temperatures above 650 K, was  $h_O/h_{\text{Fe}} = 3.45 \pm 0.10$  and next to the 44 and 51 eV peaks a 47 eV peak was observed. When the reduction was interrupted at 575 K after the fast reduction stage  $h_O/h_{\text{Fe}} = 3.9 \pm 0.2$  was measured and no 47 eV peak was observed. After reduction the crystal was sometimes sputtered. Fig. 3a shows a sputter profile after reduction at 575 K interrupted after the fast stage, fig. 3b shows the corresponding peak ratio  $h_O/h_{\text{Fe}}$  as a function of sputter time. There is an enrichment of iron(-oxide) in the outer layers, but there is also more iron in deeper layers than after deposition of iron; when a

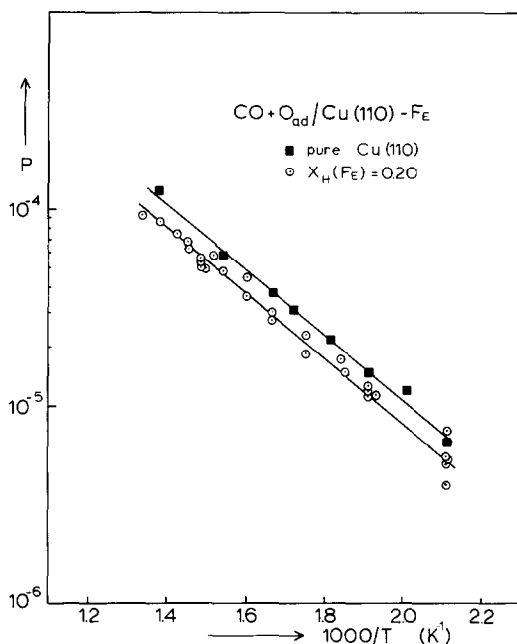


Fig. 2. Arrhenius plot of the reaction probability  $P$  of the second stage for the reaction of CO with adsorbed oxygen.

CO-reduction is performed at higher temperatures the segregation is even more significant. The  $h_O/h_{Fe}$  peak ratio is constant and equal to 3.45 from 300 until 6000 s sputtering. After high temperature reduction about the same ratios are observed from 600 s sputtering; until this time the ratio is lower. The areas underneath the sputter profiles were proportional to the values of  $\delta\psi_{Fe}$  after deposition (i.e. the total amount of iron present [6]) within experimental error whether iron was oxidized and reduced or not. Fig. 4a shows the LEED pattern of a surface which has been exposed to CO until the final slow reduction stage began. After prolonged reduction at high temperatures no pattern was observed at all. Fig. 4b shows the LEED pattern of the clean Cu(110).

### 3.1.2. Repeated admittance of CO

When Cu(110)-Fe was oxidized, again reduced, reoxidized and so on, the kinetics of the CO-reduction and the LEED pattern after the fast stage, changed. After about four cycles all observations reproduced well. Fig. 5 shows  $\delta\Delta$  as a function of the CO-exposure at different temperatures for this situation. The similarity with the reduction for pure Cu(110) is now much

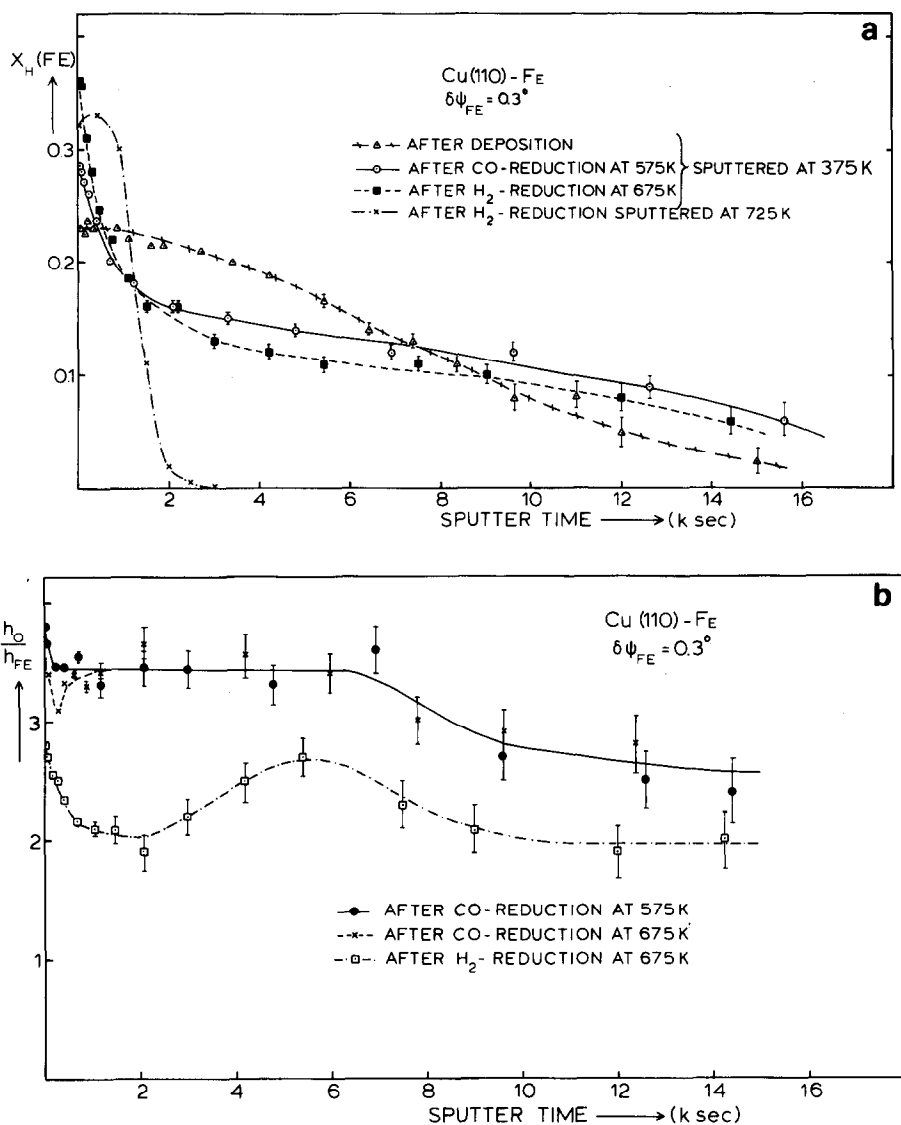


Fig. 3. (a) Iron mole fraction  $x_H(Fe)$  and (b) peak ratio  $h_O/h_{Fe}$  as a function of sputter time after reductions interrupted at various stages.

greater since the fast stage lasts about as long. The reaction rates of the fast stage are equal to those observed during the first admittance of CO; again after completed reduction  $h_O/h_{Fe} = 3.45 \pm 0.10$ , a 47 eV peak and no LEED pattern are observed. Immediately after the fast reduction stage a LEED

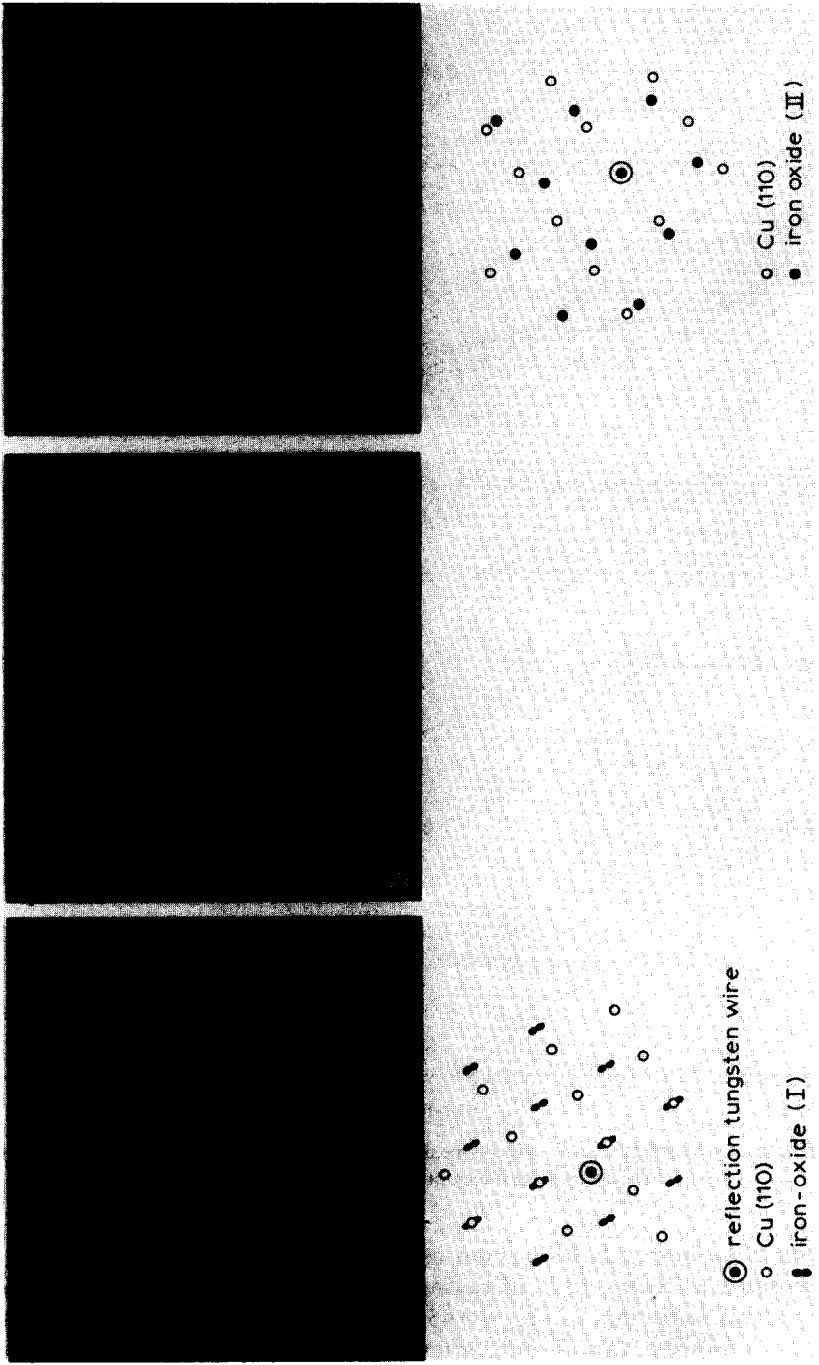


Fig. 4. LEED pattern (a) after the second stage of the first CO reduction, (b) of clean copper and (c) after the second stage of a CO reduction after more than three oxidation–reduction cycles.

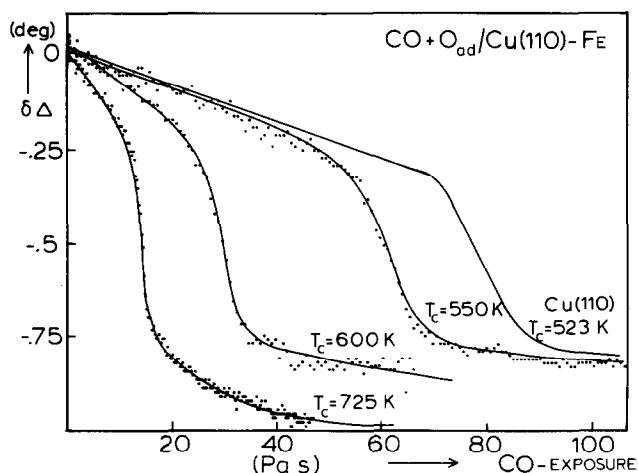


Fig. 5.  $\delta\Delta$  versus CO-exposure after more than three oxidation–reduction cycles to fully oxidized Cu(110)–Fe surface alloys at  $x_H(\text{Fe}) = 0.20$  and different temperatures. Solid lines denote solution of eqs. (1)–(5).

pattern, essentially different from the one observed after the first CO-exposure, is observed which is shown in fig. 4c.

### 3.2. Interaction with $H_2$

The interaction of hydrogen with fully oxidized Cu(110)–Fe surface alloys or surfaces prereduced with CO is studied at pressures from  $10^{-2}$  to 1 Pa and crystal temperatures of 575–725 K. After very large exposures – the reaction with oxygen fades away very slowly – all oxygen can be removed. The reaction showed poor reproducibility; fig. 6 shows the reaction curve that was commonly observed after prereduction by CO. There are three stages discernible. First there is a rather fast reduction until point D, then the reaction almost vanishes, but suddenly the rate increases again at point E (third stage) and then the reaction tails off slowly. (The nomenclature for these stages is taken from ref. [2].) However it appeared that sometimes no slow stage was present and an almost constant reaction rate was measured. Upon exposure of  $H_2$  without prereduction with CO in addition a slow stage was observed first.

As has been pointed out in the former section the kinetics of the CO-reduction changed when multiple reduction cycles were performed. This is also observed for the  $H_2$ -reduction, but less pronounced. The reaction rate of the first, relative fast stage decreased with the number of  $H_2$ -exposures as did the total amount of oxygen removed in this stage. To determine the dependence of the rate of this stage on the hydrogen pressure only measurements after about

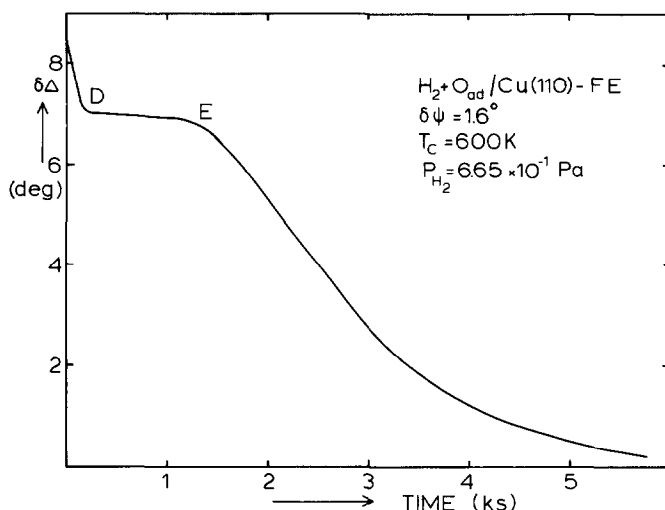


Fig. 6.  $\Delta\Delta$  versus time during  $H_2$ -exposure to a Cu(110)-Fe surface at  $T_c = 600$  K,  $p_{H_2} = 0.66$  Pa and  $\delta\psi_{Fe} = 1.6^\circ$ .

three cycles could therefore be used. Still no highly reproducible data could be gathered this way at all amounts of iron studied ( $0.1^\circ \leq \delta\psi_{Fe} \leq 1.6^\circ$ ). The orders found, ranged from 0.3 to 0.8. The reaction probability  $P$  – defined as the number of oxygen atoms removed per incoming hydrogen molecule – observed at a pressure of  $1.33 \times 10^{-2}$  Pa was about  $1 \times 10^{-6}$ . The AES oxygen to iron peak ratio at point D is independent of the amount of iron deposited, its value is equal to  $h_O/h_{Fe} = 2.8 \pm 0.1$ . Iron has segregated to the surface and the iron mole fraction  $x_H(Fe) = 0.34 \pm 0.02$  is independent of the temperature of reduction. Fig. 3a shows the sputter profile taken at this point at 375 K and fig. 3b shows the peak ratio  $h_O/h_{Fe}$  as a function of sputter time.

The increase of the iron mole fraction at the surface after reduction with  $H_2$  is rather surprising. A similar increase of  $x_H(Fe)$  was observed when the crystal temperature was increased to 725 K after an oxidation or a CO-reduction at or below 675 K, suggesting that this segregation was purely thermodynamically induced. To investigate this a crystal was sputtered after  $H_2$ -reduction until point D at 725 K instead of 375 K. As can be seen from fig. 3a no more iron is detected after only 3000 s of sputtering and it seems as if only a small amount of iron was present initially. Yet an identical amount of iron was deposited as in the crystal sputtered at 375 K.

No segregation was observed when – after an oxidation or CO-reduction at or below 675 K – the crystal was reoxidized at 725 K: the iron mole fraction



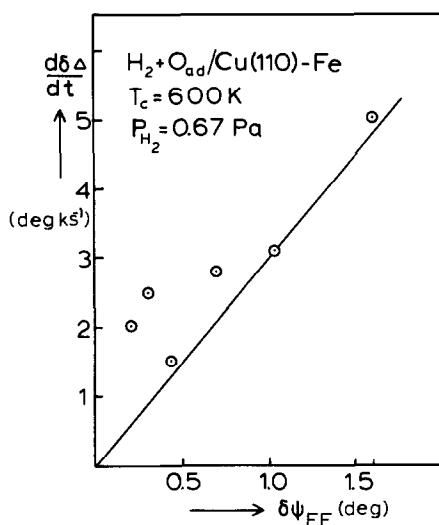


Fig. 7. Reaction rates for the reduction of an oxidized Cu(110)-Fe surface during the final  $H_2$ -reduction stage as a function of the amount of deposited iron. The drawn line is taken from the one found for the same reaction on Cu(111)-Fe [2].

observed at the surface decreased from  $x_H(Fe) = 0.34$  to 0.15. The composition remained unchanged when the temperature was increased to 775 K.

On Cu(111)-Fe it was observed that when twice as much iron was deposited the reaction rate of the final stage increased proportionally. It is interesting to compare this with the results of the same reaction on Cu(110)-Fe (fig. 7). The reaction rate of the final stage increases with the amount of iron deposited identical as on Cu(111)-Fe.

After complete reduction almost no  $h_{47}$  peak was observed and the iron mole fraction had decreased to  $x_H(Fe) = 0.10$ . The LEED pattern showed only the copper pattern, so no facets were present.

## 4. Discussion

### 4.1. CO-reduction: general features

The reduction of oxygen on Cu(110)-Fe with CO shows some similarities with the reduction of pure Cu(110). Like on Cu(110) first a slow reduction stage is observed and thereafter a fast stage, of which the rate is almost as fast as that on Cu(110) (see fig. 5). A difference is that at the moment Cu(110) is completely reduced, the reduction on Cu(110)-Fe continues slowly, though eventually it ceases before all oxygen is removed. After the reduction, no

LEED pattern is observed, but remarkably one is observed earlier, namely before the final slow reduction stage begins. Surprisingly when more oxidation and CO-reduction cycles are performed, some LEED spots which are observed first, disappear in favour of others. This observation is accompanied by a decrease in the length of the fast reduction stage which is eventually about as long as on Cu(110). This is the situation shown in fig. 5.

Whereas some LEED spots disappear and others appear, some remain. It is not difficult, examining figs. 4a, 4b and 4c, to conclude that those remaining spots originate from clean Cu(110). This means that, like on Cu(111)–Fe, copper can be reduced completely. It indicates also that the final slow reduction stage is a reduction of iron.

On Cu(111)–Fe it was shown that the LEED patterns were a superposition of patterns from clean copper and iron oxide. It is logical to assume this also for Cu(110)–Fe. Both the spots apart from the copper spots observed after the first cycle and those which show up after more cycles form a simple hexagonal pattern. The difference between them is that they are rotated about  $35^\circ$  with respect to each other. Of course the interatomic distance of the iron oxide at the surface can be derived easily from these patterns. After the first reduction cycles this distance is  $2.95 \pm 0.03$  Å, after repeated cycles it is  $3.12 \pm 0.02$  Å. Both values compare favourably with the fcc  $Fe_{1-x}O$  wüstite structure which has a hexagonal (111) plane with a spacing of 3.06 Å. As the closest packed oxygen atoms in  $Fe_3O_4$  have a spacing of 2.97 Å the initially observed oxide corresponds to this iron-oxide structure too.

The change in alignment of the oxide may be explained as follows. The angle of about  $35^\circ$  by which it rotates is equal to the angle that the diagonal of the rectangular structure of Cu(110) makes with the long side. This suggests that the rotation is related to the surface structure of copper. The final configuration of the surface is the one that is of course energetically most favourable. The fact that the oxide does not immediately take up this preferred position is easily explained when one considers that before oxidation a faceted iron structure is present, which means that every iron atom has a fixed position with respect to the copper matrix. To remove it from there may not be very easy. So initially when iron is oxidized, the iron oxide must accept a less preferred position. When iron oxide is reduced by CO and partly by  $H_2$ , after which the surface is disordered since no LEED pattern is observed, and reoxidized it will be able to take up its most stable configuration. The rotation over  $35^\circ$  emphasizes the important role that the geometry of the copper surface plays in this change. Since spots is hardly the word to use for the stripe-like appearances of the iron oxide pattern observed after a first reduction, this also shows the bad fit of this structure in the copper matrix (more specifically in the  $\langle 011 \rangle$  direction).

It is remarkable that the iron oxide fits best when its lattice parameter is precisely half the cross diagonal of the cubic unit cell (6.25 Å) of copper and

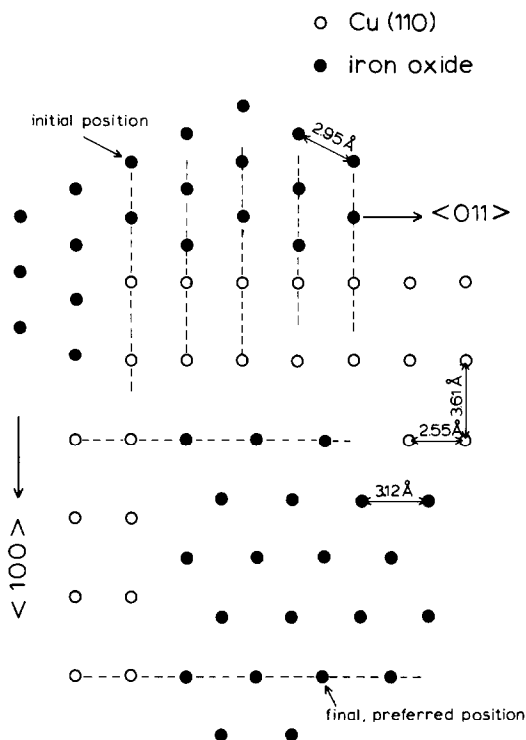


Fig. 8. The position that iron oxide takes up with respect to the Cu(110) matrix initially and after a few oxidation–reduction cycles (top view). The dotted lines show the alignment with copper.

when there is an alignment in the  $\langle 100 \rangle$  direction (see fig. 8), whereas the initial position of the iron oxide is less preferred although there is a very good alignment in the  $\langle 011 \rangle$  direction (fig. 8).

There is a significant difference in the lattice constant of the iron oxide as it is increased from initially 2.95 to 3.12 Å. This coincides with the decrease in the length of the fast CO-reduction stage, which means that the amount of oxygen that is incorporated in the iron oxide decreases each cycle. This will be an argument in the discussion for a model of the kinetics later on.

An important question is which iron oxide is observed. On Cu(111)–Fe it was determined that a peak ratio  $h_O/h_{Fe} = 3.45 \pm 0.10$  and a hexagonal lattice parameter of  $3.14 \pm 0.05$  Å corresponded to  $Fe_{0.95}O$  [2]. As these parameters are observed in the present work after a number of oxidation–reduction cycles the conclusion is that  $Fe_{0.95}O$ , wüstite, is observed. As wüstite is observed after only copper has been reduced, it means that even after thorough oxidation only wüstite is formed. This is quite different from Cu(111)–Fe where even  $\gamma\text{-Fe}_2\text{O}_3$  was observed. The peak ratios  $h_O/h_{Fe}$  observed during sputtering (fig.

3b) support the assumptions. There is no contribution of oxygen adsorbed on copper to  $h_O$ . The constant ratio of  $h_O/h_{Fe}$  of  $3.45$  during  $8000$  s sputtering confirms that throughout a rather deep surface layer a constant stoichiometry ( $Fe_{0.95}O$ ) exists.

As has already been stated an iron oxide is present after the first CO-reduction, containing more oxygen than  $Fe_{0.95}O$ . On Cu(111)–Fe a peak ratio  $h_O/h_{Fe} = 4.4 \pm 0.1$  and a hexagonal lattice parameter of  $3.01 \pm 0.05$  Å corresponded to  $Fe_3O_4$ . The observed lattice parameter of  $2.95 \pm 0.03$  Å is in accordance, but the observed peak ratio of  $3.9 \pm 0.2$  is not in accordance with an  $Fe_3O_4$  species. Therefore we assume that a species like  $Fe_{0.95}O$  is present with only some extra oxygen at the surface. The importance of the rather small lattice parameter must not be overestimated as the epitaxy of this iron oxide to copper is poor.

An unanswered question is what the continued CO-reduction must be ascribed to. The sputter profile in fig. 3b shows that near the outer surface layers oxygen is removed, but after  $1000$  s sputtering the peak ratio  $h_O/h_{Fe}$  is again equal to  $3.45$ . As a large amount of iron is near the surface layer (fig. 3a), the amount of removed oxygen is significant and apparently no perfect stoichiometry exists near the surface layer. This is in agreement with the lack of a LEED pattern. So iron is reduced a little and the  $Fe_{0.95}O$  structure is affected by CO.

Reduction of  $Fe_{0.95}O$  by CO was not observed on Cu(111)–Fe, only  $\gamma$ - $Fe_2O_3$  could be reduced to  $Fe_3O_4$ . So the possibility of reducing  $Fe_{0.95}O$  is remarkable also in view of the impossibility to reduce oxidized Fe(100) by CO [3]. However, the explanation is simple. In the temperature range where our experiments are performed wüstite itself is unstable; it will decompose into  $Fe_3O_4$  and Fe [8]. Apparently wüstite can be stabilized by the hexagonal surface structure of Cu(111) or  $Al_2O_3$  [8]; when no reasonable fit onto the substrate surface is possible the decomposition will (partly) take place. The rectangular shape of Cu(110) is responsible for this phenomenon.

The study on the reaction rate and its dependence on the temperature was concentrated on the fast reduction stage. The activation energy is equal for Cu(110) and Cu(110)–Fe which was also observed for Cu(111) and Cu(111)–Fe. This was explained by assuming that only oxygen atoms on copper sites could react with CO also adsorbed on copper sites. The decrease in reaction rate with the iron mole fraction was caused by iron oxide which reduced the total copper surface [2]. The activation energies of Cu(110)–Fe and Cu(111)–Fe are equal within error,  $31.5 \pm 0.5$  and  $31 \pm 1$  kJ/mol respectively. This emphasizes the non-plane specific behaviour of this reaction also noticed for pure copper.

#### 4.2. CO-reduction: model

The reduction of oxidized Cu(110) by CO is well understood [4] in terms of a Langmuir–Hinshelwood mechanism. First there is a slow reaction of surface

oxygen with adsorbed CO and a simultaneous migration of subsurface oxygen (unreactive towards CO) to a surface site. After completion of this stage the remaining surface oxygen is removed. It was argued in section 4.1 that the final slow reduction was an incomplete reduction of wüstite. To describe the reduction of Cu(110)–Fe in addition to the model for Cu(110) it is assumed that the destabilization of  $Fe_{0.95}O$  begins at the moment some surface oxygen is removed. Some  $Fe_{0.95}O$  decomposes into  $Fe_3O_4$  and Fe of which  $Fe_3O_4$  is reduced to  $Fe_{0.95}O$ . For clarity the reduction by CO after a few cycles will be discussed first, and thereafter the reduction immediately after the first oxidation. The reaction scheme is:

$$d\theta_s/dt = -k_1\theta_s\theta_{CO} + k_2\theta_{sub}(\theta_s^O - \theta_s) + k_3\theta_{FeO}(\theta_s^O - \theta_s), \quad (1)$$

$$d\theta_{sub}/dt = -k_2\theta_{sub}(\theta_s^O - \theta_s), \quad (2)$$

$$d\theta_{FeO}/dt = -k_3\theta_{FeO}(\theta_s^O - \theta_s), \quad (3)$$

$$\theta_{CO} = K(\theta_s^{\max} - \theta_s)P_{CO}, \quad (4)$$

$$\theta_s^{\max} = 0.5(1 - \alpha x_H(Fe)), \quad (5)$$

where  $\theta_s$ ,  $\theta_{sub}$  and  $\theta_{FeO}$  are the surface, subsurface and reacting FeO oxygen coverages,  $\theta_s^{\max}$  the maximum fraction of surface sites where CO may adsorb,  $\theta_s^O$  the maximum fraction of surface sites occupied by oxygen,  $\alpha x_H(Fe)$  is the number of sites blocked by iron-oxide crystallites and the  $k$ 's are rate constants. For the numerical fit the values for  $k_1$ ,  $k_2$ ,  $K$  and  $\theta_s^O$  of pure Cu(110) were used [4]. Fig. 5 shows the results of simulations of the reduction at three temperatures. To be able to fit we had to take a value for  $\alpha = 0.7 \pm 0.1$ , whereas on Cu(111)–Fe  $\alpha = 1.4 \pm 0.1$  was found. The difference is simply due to the difference in the number of sites  $N$  on Cu(110) and on Cu(111). Assuming that an iron atom on Cu(110)–Fe possesses the same unit area as on Cu(111)–Fe  $\alpha = 0.85 \pm 0.10$  should be expected on Cu(110)–Fe since the ratio of sites is  $N(110)/N(111) = 0.61$ . The agreement between the expected and experimental value for  $\alpha$  is satisfactory.

The reaction rate in the fast stage (when  $\theta_{sub} \approx 0$  since all subsurface oxygen is converted to surface oxygen and  $k_3\theta_{FeO} < k_1KP_{CO}\theta_s$ ) is:

$$r = -k_1K\theta_s(\theta_s^{\max} - \theta_s)P_{CO}. \quad (6)$$

The activation energy is determined by  $k_1$  and  $K$  like on Cu(110), thus the fact that the activation energies on Cu(110) and Cu(110)–Fe are equal is in agreement with the model.

To explain the reaction curves observed during the first CO-exposure it is assumed that some extra oxygen  $O^+$  is bound to iron which can easily be

removed once the surface oxygen coverage decreases. So instead of eq. (1) we have:

$$d\theta_s/dt = -k_1\theta_s\theta_{CO} + k_2\theta_{sub}(\theta_s^O - \theta_s) + k_2\theta_{FeO}(\theta_s^O - \theta_s) + k_4\theta_{O+}(\theta_s^O - \theta_s), \quad (7)$$

$$d\theta_{O+}/dt = -k_4\theta_{O+}(\theta_s^O - \theta_s). \quad (8)$$

The results of the simulation using eqs. (2)–(5), (7) and (8) is shown in fig. 1. As can be seen the model is able to fit the reaction curves. Fitting was possible with  $k_1KP_{CO}\theta_s/2\theta_{O+} < k_4 < 2k_1KP_{CO}\theta_s/\theta_{O+}$ , so no exact values for  $k_4$  could be determined. For  $\theta_{O+}$  and  $\theta_{FeO}$  respectively 0.8 and 0.4 was obtained. The activation energy of  $k_3$  was about 80 kJ/mol.

### 4.3. $H_2$ -reduction

In section 4.1 it was stated that after a pre-exposure of CO the reduction with hydrogen will start at a stage when already some wüstite has decomposed. First  $H_2$ -reduction occurs relatively fast (up to point D in fig. 6), but then the reaction rate drops quickly. On Cu(111)–Fe the same behaviour was noticed and it was ascribed to the beginning of the reduction of wüstite. This cannot be the case on Cu(110)–Fe; the nomenclature in fig. 6 therefore merely corresponds to the one of Cu(111)–Fe in the sense that it points to identical changes in reactivity.

At point D no stoichiometric iron-oxide can be present of course since wüstite is the species with the lowest oxidation state of iron. Two observations support this. The first is that there is no LEED pattern observed at point D. Secondly the peak ratio  $h_O/h_{Fe}$  during sputtering (fig. 3b) is not constant and excludes stoichiometry throughout the crystal. The value of  $h_O/h_{Fe} = 2.8$  at the surface is in accordance with the assumption that wüstite has been reduced, since  $h_O/h_{Fe} = 3.45$  corresponds to wüstite.

As for Cu(111)–Fe sudden changes in reaction rate during reduction were ascribed to transitions of iron-oxide species, one wonders what causes the decrease at point D. Two extra experiments were performed to understand this. But first we recall the following results.

The variation of  $h_O/h_{Fe}$  during sputtering of a crystal at point D is remarkable (see fig. 3b). The maximum of  $h_O/h_{Fe}$  after 6000 s sputtering suggests that oxygen bound to iron at a corresponding deep layer will hardly diffuse to the surface to be removed. In ref. [6] it was proved that during oxidation of Cu(111)–Fe not oxygen but merely iron and iron-oxide atoms are mobile. Therefore it is assumed that to become reduced iron oxide atoms must diffuse to the surface. This implies that during reduction much iron must be present at the surface as iron oxide. As at point D and after complete CO-reduction segregation of iron is observed (fig. 3a) this assumption is

strongly supported. Since this segregation is apparently limited to  $x_H(\text{Fe}) = 0.34$  (see fig. 3a) this may limit the reduction process and another diffusion mechanism must take over the oxygen transport to continue the reduction.

Apparently diffusion to the surface is slow at point D. This should also be noticed when the crystal is oxidized at point D. To investigate this an oxidation was performed at 675 K after  $H_2$ -reduction until point D, until saturation occurred, i.e. the sticking coefficient became lower than  $1 \times 10^{-4}$ . Next the vacuum chamber was evacuated and the crystal was kept at 475 K for two hours. Then oxygen was re-exposed and now an initial sticking coefficient of about  $1 \times 10^{-1}$  was observed and an amount of oxygen corresponding to half a monolayer could easily be adsorbed! Thus a slow (most probably unactivated) diffusion process had made copper sites free to read-sorb. To verify this the experiment was repeated but after oxidation at 675 K the crystal was cooled to 300 K. LEED patterns after all standard oxidation

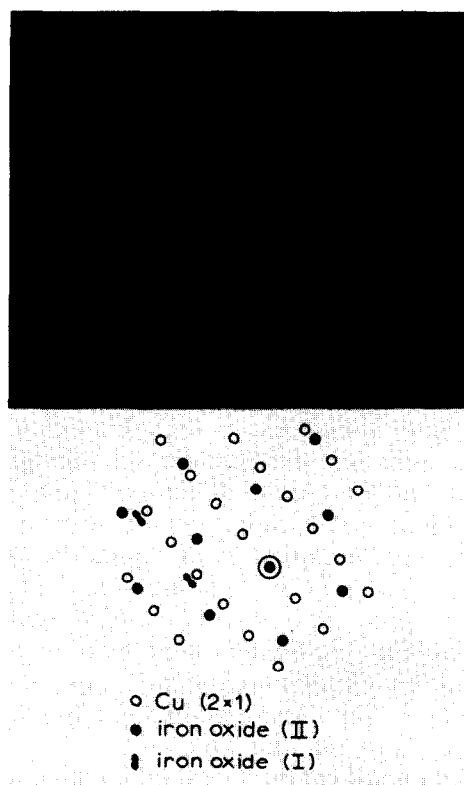


Fig. 9. LEED pattern after oxidation at 675 K immediately after  $H_2$ -reduction until point D, showing a superposition of  $\text{Fe}_{0.95}\text{O}$  and a  $(2 \times 1)$  structure of  $\text{O}_{\text{ad}}/\text{Cu}(110)$ .

experiments at 675 K had revealed a  $c(6 \times 2)$  structure [6], but instead of this a superposition of a copper  $(2 \times 1)$  structure and a wüstite structure (fig. 9) was observed. Since a  $(2 \times 1)$  structure corresponds to a less far oxidized state of copper, oxygen must have been transported to iron, which was oxidized at the expense of copper. During the relatively short oxygen exposure oxygen cannot penetrate fast enough to iron in deeper layers and therefore the oxidation will stop. This same slow oxygen transport will then limit the reduction rate at point D.

Accurate determinations of the order of the reaction on the hydrogen pressure were difficult due to the decrease of the reaction rate with the number of cycles and the overall irreproducibility. An order of a 0.5 seems most probable from the experimental values. The same order was found for Cu(111)–Fe and it implies that iron facilitates hydrogen dissociation [2,4].

The sputtering of an alloy at 725 K incompletely reduced with  $H_2$  (see fig. 3a) has an obvious explanation. When it would have been sputtered at 375 K iron would be removed after more than 20 000 s (see fig. 3a). At 725 K all iron has disappeared after 3000 s. It can only be explained when iron oxide segregates during sputtering.

Since after reoxidation at 725 K no segregation is observed, wüstite itself does not segregate, it does only when it is oxygen deficient.

The final stage of hydrogen reduction is not thoroughly investigated because of the large exposures necessary. Although the scatter of the reaction rates is large, the dependence of them on the amount of iron deposited is the same as on Cu(111)–Fe [2].

## 5. Conclusion

Copper in a thoroughly oxidized Cu(110)–Fe crystal can be reduced completely by CO. Since a small part of  $Fe_{0.95}O$ , which is the only iron oxide that can be formed even after severe oxidation, decomposes into  $Fe_3O_4$  and Fe, also some iron can be reduced. Initially  $Fe_{0.95}O$  takes up a different orientation with respect to the copper matrix than after a few cycles of (incomplete) reduction and oxidation. The less preferred orientation is induced by the presence of iron facets before the oxidation. The reaction with CO can be simulated with a model which is an extension of the model for the same reaction on pure Cu(110). The reaction takes place on copper sites and the influence of iron oxide is mainly to reduce the copper surface; this reduction factor is the same as on Cu(111)–Fe when the density of copper atoms on both copper surfaces is taken into account.

With hydrogen all oxygen can be removed from a Cu(110)–Fe crystal. The reaction rate which is first relatively fast decreases due to a slow transport of oxygen to the surface, but thereafter it increases again. When  $Fe_{0.95}$  is oxygen



deficient – due to CO-reduction, a partial H<sub>2</sub>-reduction or incomplete oxidation – it segregates at 725 K. This becomes more evident when it is sputtered at 725 K since then it is removed much faster than at 375 K.

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