

THE ADSORPTION AND DECOMPOSITION OF CARBON MONOXIDE ON Ni(100) AND THE OXIDATION OF THE SURFACE CARBIDE BY OXYGEN

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The interaction of carbon monoxide with Ni(100) has been studied by ellipsometry and Auger electron spectroscopy. Bombardment by electrons of a relatively high energy (2500 eV) leads to the disproportionation of the adsorbed CO ($2\text{CO}_{\text{ad}} \rightarrow \text{C}_{\text{ad}} + \text{CO}_{2\text{g}}$). The rate of oxidation of this surface carbide is

$$-dh_C/dt = k_0 h_C P_{\text{O}_2}^n \exp(-E_{\text{act}}/RT),$$

where h_C is the carbon 272 eV Auger peak height, $n=0.5$ and the apparent activation energy $E_{\text{act}} = 13.3$ kcal/mole. This relation is valid at 200-400°C and at oxygen pressures of 5×10^{-9} - 8×10^{-7} Torr.

1. Introduction

The interaction of carbon monoxide with nickel single crystals has been studied by many authors [1-24]. It has been observed that the adsorption of CO on nickel is completely reversible below temperatures of 180°C, but that at more elevated temperatures, exposure of monocrystalline Ni surfaces to CO results in the buildup of carbon. Below 180°C buildup of carbon can also be brought about by the incidence of electrons of sufficiently high energy [22-25]. A number of theoretical analyses have dealt with the interaction of CO with transition metal surfaces below 280°C [27]. Disproportionation of CO ($2\text{CO} \rightarrow \text{C}_{\text{ad}} + \text{CO}_{2\text{g}}$) is thermodynamically favoured, but there is evidence that dissociative adsorption is also possible, with formation of a Ni-C and a Ni-O bond ($2\text{Ni} + \text{CO} \rightarrow \text{Ni-C} + \text{Ni-O}$) [26]. The surface carbon is carbidic and does not react to graphite upon heating in vacuum, but rather diffuses into the bulk [28]. According to Coad and Rivière [33] nickel carbide is not stable above 400°C and most of the evidence suggests that it starts to decompose

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slightly below that temperature. During decomposition free carbon is formed.

The oxidation of the carbidic surface by oxygen [34,35] has been investigated less extensively than the reaction with hydrogen [2,27–32].

In the present paper we report our results on:

- (i) the adsorption of CO on Ni(100) at room temperature, and the influence of surface carbon on the extent of adsorption;
- (ii) the electron beam induced disproportionation of adsorbed CO;
- (iii) the reactivity of the surface carbon thus obtained with oxygen at temperatures of 200–500°C and oxygen pressures of 5×10^{-9} – 8×10^{-7} Torr.

Ellipsometry, which does not disturb the adsorbed species, was used to monitor the adsorption and decomposition of CO. Auger electron spectroscopy was utilized to obtain the oxidation reaction rates and to determine the surface composition of the Ni crystal.

2. Experimental

Most of the experiments were carried out in a Riber UNI-5 system described previously [36], with facilities for AES–LEED, simultaneous ellipsometry, mass spectrometry and argon ion bombardment. The base pressure was about 10^{-10} Torr. The crystal was the same as the one used in previous experiments [37,38]. Ellipsometry was done at an angle of incidence of 68.2° and at a wavelength of 6328 Å with either two-zone or off-null irradiance measurements.

The remaining experiments were done in a Varian UHV system with the same facilities and with the same crystal as mentioned above. This system had a base pressure of 5×10^{-11} Torr. The Auger spectra were obtained in their usual first derivative form $E dN(E)/dE$ using a cylindrical mirror analyser (Varian 981-2707, resolution better than 0.3%), with an on-axis electron gun (Varian 981-2713). This electron gun was adjusted to yield an anode current of 260 μ A at an energy of 2.0 keV and an electron beam diameter smaller than 0.12 mm at the sample plane. A modulation frequency of 17 kHz and a modulation voltage of 5 or 10 V peak to peak were used. The spectrometer had an analysis range for Auger electrons of 0–3000 eV. A Varian ion bombardment gun and control unit (model 981-0043 and 981-0046) were used for argon ion sputtering. The entire system was bakable up to 250°C. The gases used, i.e., argon (purity 99.999%), oxygen (99.995%) and carbon monoxide (99.99%) were manufactured by L'Air Liquide.

After installation in one of the UHV systems and bake-out the crystal was subjected to the cleaning procedure described by Schouten [39].

3. Results

3.1. Adsorption of CO on Ni(100) at room temperature

The change in the ellipsometric parameter Δ , $\delta\Delta = \bar{\Delta} - \Delta$, where $\bar{\Delta}$ is the value for the clean surface and Δ is the value for the surface with adsorbate, is shown in fig. 1. At CO pressures from 6×10^{-9} to 6×10^{-8} Torr the coverage saturates after an exposure of about 6 L (1 L = 10^{-6} Torr s = 1.33×10^{-4} Pa s). This constant saturation coverage ($\delta\Delta_{\max} = 0.25 \pm 0.05^\circ$) corresponds to about 0.6 of a monolayer [19–22]. The change in Δ could be described by:

$$\delta\Delta = \delta\Delta_{\max} [1 - \exp(-kt)], \quad (1)$$

with $k = k_0 p_{\text{CO}}$ (see fig. 2). The initial sticking coefficient was about unity. The fact that the above relation, valid for Langmuir kinetics, holds allows us to infer with some confidence that $\delta\Delta$ is linearly proportional to the CO coverage with θ_{CO} (monolayers) $\approx 2.4 \delta\Delta$ (deg).

No significant changes in ψ were observed during our experiments.

3.2. Electron beam induced disproportionation of CO on Ni(100)

After evacuation the adsorbed CO was subjected to bombardment with 2.5 keV electrons from the AES electron gun. This treatment caused the CO to disproportionate, leaving a surface with carbon but very little oxygen [22]. Monitoring the oxygen AES peak height showed a steady decrease, while in another run the carbon peak height was observed to remain constant (fig. 3). When we prepared a surface with half a monolayer of carbide by means of the thermal decomposition of ethylene [40] we observed, however, a carbon peak that was about 1.7 times as large as the one measured after electron bombard-

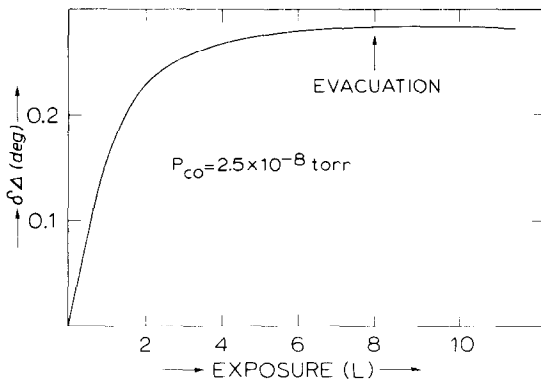


Fig. 1. Adsorption of carbon monoxide on Ni(100) at room temperature; $\delta\Delta$ as a function of CO exposure.

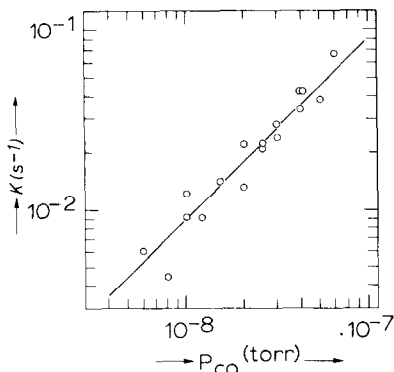


Fig. 2. Rate constant k for CO adsorption on Ni(100) at room temperature as a function of CO pressure.

ment of adsorbed CO. The disproportionation was in most cases accompanied by a simultaneous decrease to zero of $\delta\Delta$ indicating that carbon coverages of up to about one third of a monolayer have no effect on Δ at the wavelength used (6328 Å). In some cases, however, $\delta\Delta$ decreased to a non-zero value, whereas AES indicated that complete disproportionation had occurred. The difference turned out to be caused by an incomplete overlap of the area of the crystal onto which the electron beam was focused, and the area where the CO coverage was measured, i.e., the area irradiated by the ellipsometer light beam.

Defocusing the electron gun caused $\delta\Delta$ to decrease to zero (fig. 3). The C 272 eV AES lineshape indicated that the carbon deposit thus formed was carbidic.

It was possible to perform a second CO adsorption/disproportionation cycle on the surface. The amount of CO adsorbed in this case was roughly half of that taken up by the clean surface (fig. 4). The results described thus far have been obtained with the Riber UHV system.

3.3. Reaction of the surface carbon with oxygen

The oxidation reaction was studied in both the Riber and the Varian UHV system. In the Riber system the carbon was deposited as described above. In the Varian system the reactivity of a (carbidity) carbon contamination—typically about a quarter of a monolayer—was studied. In both UHV systems the carbon layer was disordered since the LEED pattern showed no superstructure.

The reaction of oxygen with the surface carbon resulting either from the electron beam induced decomposition of CO (Riber UHV system) or already present (Varian UHV system), was studied at crystal temperatures between 200 and 500°C, oxygen pressures of 5×10^{-9} to 8×10^{-7} Torr and initial carbon coverages of 0.05 to 0.3 monolayers.

Interaction with oxygen caused the carbon Auger peak height to decrease,

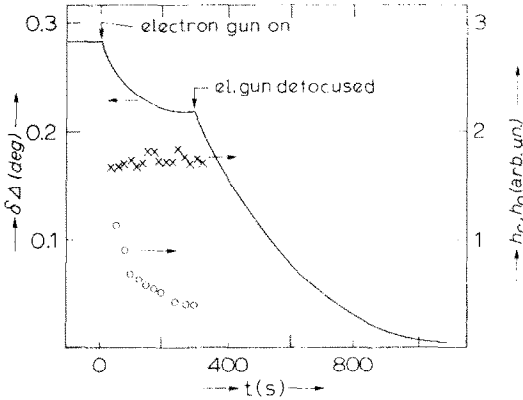


Fig. 3. Electron beam induced disproportionation of CO on Ni(100), with the effect of defocusing the electron beam: (—) $\delta\Delta$; (x) h_C (272 eV); (O) h_O (512 eV).

cf. fig. 5 (lower curve) which shows a semi-logarithmic plot of the carbon peak height versus time. The apparent increase in the reaction rate constant is caused by the fact that the true secondary background of the Auger spectrum varies with energy [41]. The insert in fig. 5 shows that the measured peak height $h = a + b - c$, while the true peak height $h_C = a + b$. Therefore $h_C = h + c$, where c is the increase in background signal between the peak and the valley of the Auger line. When this correction is made the upper curve in fig. 5 is obtained. The correction was found to be necessary for both the RFA (Riber) and the CMA (Varian) measurements.

During oxygen exposition the carbon 272 eV peak was continuously scanned,

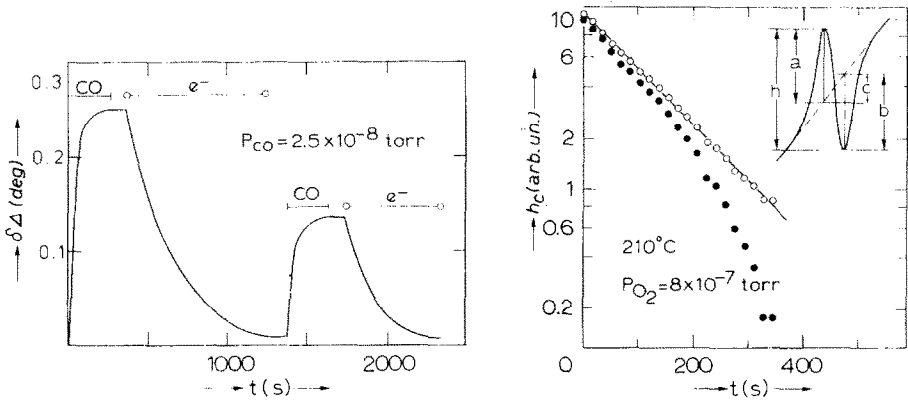


Fig. 4. The effect on $\delta\Delta$ of two CO adsorption/electron beam induced disproportionation cycles.

Fig. 5. Oxidation of the surface carbide on Ni(100): (●) h_C (272 eV) not corrected for background signal; (○) h_C corrected for background. Insert: explication of background correction, see text.

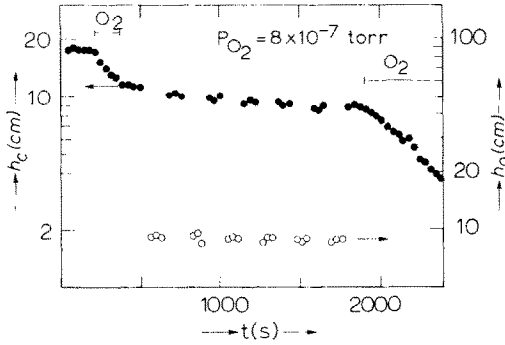


Fig. 6. Oxidation of the surface carbide on Ni(100): (●) h_C (272 eV); (○) h_O (512 eV).

each scan taking about half a minute. Operation of the AES electron gun did not influence the reaction rate.

Fig. 6 shows that on admission of oxygen the reaction started without an observable induction time. Evacuation caused the reaction to stop abruptly, while on readmission of oxygen the oxidation restarted instantaneously with the same rate constant as before the interruption. The slight decrease in the carbon peak height can be attributed to a small O_2 background pressure.

The kinetics of the reaction have been found to obey an empirical rate equation of the form:

$$-dh_C/dt = ah_C, \tag{2}$$

where

$$a = \alpha_0 p_{O_2}^n \exp(-E_{act}/RT). \tag{3}$$

This rate equation was valid for temperatures of 200–400°C, oxygen pressures

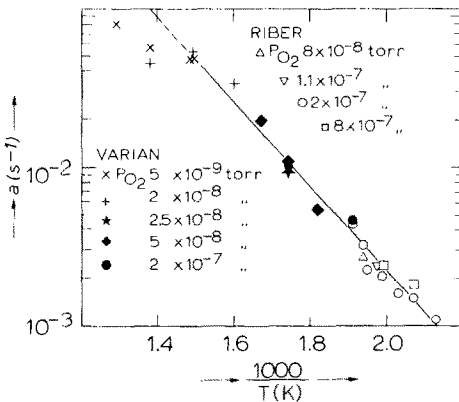


Fig. 7. Arrhenius plot of the oxidation rate; $a = \alpha(2 \times 10^{-7}/p_{O_2})^{1/2}$, cf. eq. (2).

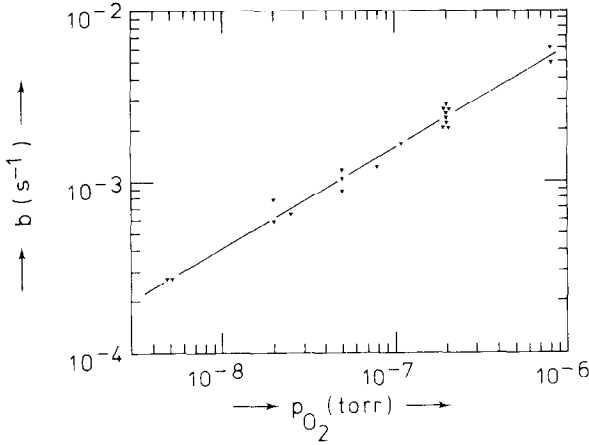


Fig. 8. Pressure dependence of the oxidation rate, scaled to constant temperature (503 K); $b = \alpha \exp[13.3R^{-1}(1/503 - 1/T)]$. The slope of the line is 0.57.

of 5×10^{-9} – 8×10^{-7} Torr and carbon coverages of 0.05–0.3 monolayers. Using a least squares procedure for simultaneously determining the best values for n and E_{act} we obtained $n = 0.57 \pm 0.1$ and $E_{act} = 13.3 \pm 1.5$ kcal/mole. Fig. 7 shows an Arrhenius plot of $\alpha(2 \times 10^{-7}/p_{O_2})^{1/2}$.

The three data points at $t > 400^\circ\text{C}$ do not fit, which is not surprising, considering that the incident flux of oxygen atoms from the gas phase is of the same order of magnitude as the number of carbon atoms removed per second

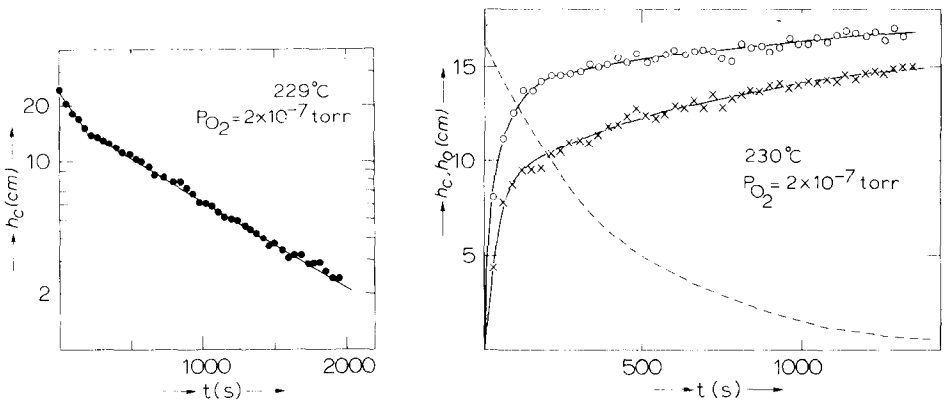


Fig. 9. Oxidation of the surface carbide obtained by means of two CO adsorption/electron beam induced disproportionation cycles.

Fig. 10. Growth of the oxygen AES peak height on clean and carbide covered Ni(100): (O) h_O on clean Ni(100); (X) h_O on carbide covered Ni(100); (---) h_C .

per cm^2 at the start of the reaction. These points were therefore not considered in the calculation of n and E_{act} .

Fig. 8 illustrates the pressure dependence of the reaction rate at $t < 400^\circ\text{C}$. The rate constants b have been calculated for 230°C using:

$$b = \alpha \exp[13.3R^{-1}(1/503 - 1/T)].$$

When carbon had been deposited by two CO adsorption/disproportionation cycles the oxidation reaction seemed to proceed in two stages (fig. 9), a fast one and a slower one. The transition occurred when about a third of the initial amount of carbon had been removed. Neither rate constant, however, was in agreement with the one found for carbon deposited by means of a single adsorption/decomposition cycle, and the reproducibility was poor.

After the reaction there was always about half a monolayer of oxygen present on the surface. This coverage was established by comparing the O/Ni AES peak height ratio to $h_{\text{O}}/h_{\text{Ni}}$ for a clean surface exposed to 5 L oxygen at room temperature, and therefore covered with half a monolayer of chemisorbed oxygen [42].

Fig. 10 shows the buildup of oxygen on the surface during the reaction with carbon, the oxidation of a clean Ni surface and the decrease of the amount of carbon, all at the same temperature and oxygen pressure.

4. Discussion

Madden and Ertl [23] have provided convincing evidence that electron bombardment of CO covered Ni(110) causes the CO to decompose, leaving a surface with atomically dispersed carbon and oxygen. Concerning Ni(100), however, the literature is still ambiguous on whether electron bombardment results in the decomposition of adsorbed CO or whether disproportionation ($2\text{CO}_{\text{ad}} \rightarrow \text{C}_{\text{ad}} + \text{CO}_{2\text{g}}$) takes place.

At first sight our results would seem to favour dissociation ($\text{CO}_{\text{ad}} \rightarrow \text{C}_{\text{ad}} + \text{O}_{\text{g}}$) since the carbon peak height, and therefore presumably the amount of carbon, remains constant during the electron bombardment. When we prepared a surface with 0.5 monolayer of carbidic carbon by means of the thermal decomposition of ethylene, however, we found that this surface gave rise to a carbon AES peak that was 1.7 times as large as the one obtained after the electron bombardment of adsorbed CO. This observation indicates that after the electron bombardment, which started with 0.6 monolayers of CO, we ended up with 0.3 monolayers of surface carbide. This favours disproportionation.

As it turns out there is quite a large difference between the AES lineshape of carbon in CO and carbon as a surface carbide [43]. By a most unfortunate coincidence this difference in lineshape results (under our experimental conditions) in an AES peak height in the differentiated spectrum that is exactly

twice as large for carbidic carbon as for carbon in adsorbed CO, assuming equal coverages. Therefore, as the disproportionation proceeds, the decrease of the total number of carbon atoms on the surface is exactly compensated for by the increase in peak height caused by the carbon atoms going from CO carbon to carbide carbon. We therefore conclude that on electron bombardment of CO adsorbed on Ni(100) the CO disproportionates into surface carbide and CO₂:



Fleisch et al. [19] report that CO exposure to a surface contaminated by about half a monolayer of carbon results in deposition of further carbon, which they ascribed to a disproportionation reaction. We did not observe a different behaviour between CO adsorption on a clean surface and on a carbon covered surface. On the contaminated surface, however, less CO could be adsorbed than on the clean surface. Accordingly, sites able to adsorb CO are partially blocked by adsorbed carbon.

The rate of oxidation of the surface carbide appeared to be first order with respect to carbon coverage. The same result was obtained by Horgan and Dalins [34] for graphitic monolayers on Ni(111) and by Sau and Hudson [35] for carbidic monolayers on Ni(110). In both these cases, however, the oxidation rate was found to be linear with oxygen pressure, whereas we found a $p_{\text{O}_2}^{1/2}$ dependence, which indicates a reaction with dissociated (atomic) oxygen although a reaction with a molecular species is not unequivocally excluded [34].

To explain our observations we propose the following reaction mechanism:



The result of reactions (5) and (6) is a mobile hot [44] precursor (O_{ad}^*), the concentration of which is proportional to $p_{\text{O}_2}^{1/2}$. These O_{ad}^* are supposedly thermally non-equilibrated atoms that move along the surface with high parallel velocity [44]. They then react with the surface carbon atoms to form CO_{ad} , which subsequently desorbs (8). Since the reaction rate is proportional to $[\text{O}_{\text{ad}}^*] [\text{C}]$ this explains the observed dependence of the reaction rate on $p_{\text{O}_2}^{1/2} h_{\text{C}}$.

During the oxidation oxygen is deposited on the surface. Fig. 10 shows that the rate of oxygen buildup is somewhat smaller than on the clean surface. It is much faster, however, than the rate of carbon removal. Since the reaction stops instantly on evacuation this surface oxygen must be unreactive towards the surface carbide. We therefore assume a separate adsorption reaction (9) of the

Ni surface which proceeds more or less independently from the oxidation of the surface carbon and results in an immobile chemisorbed oxygen species (O_{ad}). This oxygen chemisorption reaction, eqs. (5) and (9), is thought to involve a molecular precursor (O_{2ad}^*) since the adsorption rate is known to be linear with respect to p_{O_2} [42].

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