Segregated carbon on Pt$_{10}$Ni$_{90}$(100) studied by scanning tunneling microscopy

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Scanning tunneling microscopy is used to study the arrangement of segregated carbon atoms with atomic resolution. Individual carbon atoms are visible only under special tip conditions, while they normally do not directly appear on STM topographs. Under all tip conditions, carbon atoms affect the corrugation of their metal neighbours, reducing the apparent height by 20 to 40 pm in the p(2 × 2) and 40 to 70 pm in the c(2 × 2) superstructure. Therefore the existence, structure and amount of carbon can be also derived from images without directly visible carbon atoms. A substrate lattice distortion in regions of the carbon c(2 × 2) superstructure was observed, exhibiting areas of the p4g structure known from earlier LEED studies of Ni(100).

Carbidic carbon on transition metal surfaces plays an important role in catalytic reactions on these surfaces. Since Pt–Ni alloys are of special interest as catalysts for some hydrocarbon hydrogenation reactions, the study of carbon on Pt–Ni surfaces is not only of academic interest, but it may also provide interesting information for understanding these catalytic processes.

While little work has been done on carbon adsorption or carbon segregation on Pt–Ni alloy surfaces, carbon on Ni(100) has been studied by LEED rather extensively more than a decade ago [1–4], finally leading to the conclusion that the surface saturated with carbidic carbon exhibits a c(2 × 2) carbon structure with carbon atoms in fourfold hollow sites of the substrate lattice. In this structure, the substrate atoms are shifted laterally and thereby increase the distance from their next neighbour carbon atoms [4,5]. The substrate distortion reduces the c(2 × 2) symmetry of the system to p(2 × 2), the surface space group is p4g. The vertical position of the carbon atoms is only 12 ± 4 pm above the topmost Ni layer; comparison with the nearest neighbour carbon–nickel distance of 182 pm shows that the carbon atoms are essentially in the same plane as the first metal monolayer [5]. Further studies of this structure using SEELEFS [6,7] and SEXAFS [8] agree with the nearest neighbour carbon–nickel distance given in refs. [4] and [5].

While carbon has been formed from ethylene or CO decomposition for the studies in refs. [4] and [6–8], the present work deals with carbon segregated from the bulk of the crystal. This has the advantage that the surface structure forms at higher temperatures (above 700 K) than those used for ethylene or CO decomposition (usually below 600 K to avoid carbon diffusion into the bulk). Therefore the surface structure examined in our study is near thermodynamic equilibrium at least at high temperature, while structures from reactive adsorption of ethylene may be kinetically limited. The disadvantage of the segregation approach is the limited range of surface concentrations accessible with the given bulk impurity content of one crystal. This problem is not severe for an STM study, however, since imaging in real space permits to derive local information from small regions with different local carbon concentrations.

On the Pt$_{10}$Ni$_{90}$(100) surface, carbon has a strong influence on the surface composition: The
clean surface exhibits Pt segregation to the first monolayer, yielding a surface concentration of approximately 24% Pt, the second monolayer is depleted of Pt [9]. This oscillatory segregation profile is due to the interplay of surface free energy and bulk order [10,11]. The presence of segregated carbon reduces the Pt concentration of the first monolayer to slightly below the bulk composition at approximately 25% of a full monolayer carbon after annealing at 770 K [12,13]. This change of surface composition is attributed to the larger affinity of carbon towards Ni compared to Pt [11].

Our results were achieved using a commercial scanning tunneling microscope (Omicron micro-STM) operated in constant current mode. In addition to the viton stack of the STM head, the whole vacuum chamber is suspended by a combined spring-elastomer system for improved vibration isolation at low frequencies [14]. The tip was electrochemically etched from tungsten wire and cleaned in vacuum by field evaporation (300 V) and voltage pulses (3 to 10 V) while tunneling. All STM images are constant current topographs obtained with negative sample bias. Sample preparation and STM analysis were done in ultra-high vacuum at a base pressure below 1 × 10^{-10} mbar.

We have used two Pt_{10}Ni_{90}(100) single crystals with different bulk carbon content, cleaned by sputtering (500 eV Ne^+, Ar^+ or Xe^+, approx. 2 µA/cm^2) and annealed (≈ 800 K) before the STM measurements. For reaching low surface concentrations of carbon, sputter cleaning at elevated temperatures (≈ 800 K) for 10 to 50 h was used to deplete carbon in a thick subsurface region. Although such a treatment may cause compositional variations in alloys due to preferential sputtering and diffusion [15], we believe that these effects are not very pronounced on this surface which shows weak Pt segregation [12,13] counteracting the mass-effect in preferential sputtering.

Apart from scanning tunneling microscopy, the samples were repeatedly examined by Auger electron spectrometry (AES) using a cylindrical mirror analyzer. Since AES does not show any carbon on the freshly sputtered surface, we have estimated the bulk carbon content from AES measurements of segregated carbon, assuming that the relative carbon depletion caused by high-temperature sputtering on the surface reflects the subsurface compositional changes. With diffusion coefficients of carbon in Ni [16] this estimate yields an atomic concentration of 10^{-5} to 10^{-4} carbon in the bulk.

Figs. 1 and 2 show two STM images of a Pt_{10}Ni_{90}(100) single crystal, which have been obtained on nearby surface regions within a few minutes. Since the crystal was at room temperature and the background pressure was sufficiently low, the surface structure and composition in these images are identical. Both images show a few close-packed rows of atoms slightly protruding from the surface, which are shifted into a bridge position of the underlying second monolayer [17]. As our STM studies show, this “shifted row” reconstruction exists with or without carbon on the surface, but it mainly depends on the Pt-concentration [18]. Therefore, we shall not focus on this reconstruction here; we only note that the shifted rows are nonperiodic features which offer a good way to test the STM tip and exclude contrast reversal and effects of multiple tips.

Both figs. 1 and 2 also show variations of brightness (i.e. vertical tip position) in the regions between the shifted rows. Comparing images of surfaces with different carbon concentration, we found out that the size of the darker (apparently lower) regions increases with the amount of carbon on the surface, whereas it does not correspond to either Pt or Ni concentration in the first monolayer (e.g. at low C concentration, where we should find approximately 25% Pt in the first monolayer). In other words, we did not find any difference of apparent height between Pt and Ni.

The only difference between figs. 1 and 2 is the existence of additional bright spots in fig. 1. These spots appear in fourfold hollow sites of the substrate lattice, but they do not look like normal STM images of atoms but rather fuzzy at their top, with abrupt edges. These spots have some similarity with STM images of carbon atoms on Al(111) obtained by Brune et al. [19]. In both cases, the “bright” atoms show indications of an unstable (possibly bistable) behaviour of the feed-
Fig. 1. Atomically resolved STM constant current topograph of the (100) surface of a Pt$_{10}$Ni$_{90}$ single crystal. Tunneling voltage 2 mV, current 14 nA, size $15 \times 15$ nm$^2$. The bright spots in the darker areas (diamond pattern) are segregated carbon atoms, furthermore several "shifted rows" are visible (arrows). An enlarged portion is shown at the bottom. A comparison with the schematic drawing of the atom arrangement shows the different apparent height (brightness) of metal atoms depending on the number of carbon nearest neighbours. Unit cells of p(2 x 2) structure are indicated by squares; c(2 x 2) structure is found, e.g. near the bottom right corner of this frame.
back loop, although our images do not appear as noisy as those in ref. [19] owing to the behaviour of our STM control unit, which takes an average value of several readings if feedback conditions are unstable.

Since the bright spots appear in a concentration (20% of a monolayer, i.e. 40% of a full e(2x2) coverage) compatible with Auger measurements of the carbon concentration, and since the sample is otherwise clean, we conclude that the bright spots are due to single atoms of segregated carbon. However, the mechanism responsible for direct detection of the carbon atoms cannot be explained by any standard STM theory, since the cores of the carbon atoms are virtually in plane with the neighbouring metal atoms [4,5]. Furthermore, images like fig. 1 usually do not occur even if the same tunneling voltage and current as used for this image are chosen, and the visibility of the carbon atoms disappears after the tip apex is reconditioned by a voltage pulse, although atomic resolution is preserved. This means that imaging of C atoms on this surface needs special tip conditions. Possibly some kind of chemical interaction between the foremost tip atom and the sample is required as recently proposed in the case of “chemically resolved” scanning tunneling microscopy [20]. Such a mechanism, e.g. an adsorbate hopping back and forth between tip and sample, may also explain the instable imaging conditions of the carbon atoms.

Fig. 1 also shows that the apparent height (brightness) of metal atoms is reduced by neighbouring carbon atoms, while it remains largely

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**Fig. 2.** STM image taken a few minutes after fig. 1, after the tip has been reshaped by a voltage pulse. Tunneling voltage/current: 0.5 mV/5 nA. The brightness of the lower terrace (bottom quarter of the image) has been increased to make it visible in spite of the high image contrast used. A section profile between the two arrows clearly shows the different apparent height levels of metal atoms without neighbouring carbon (“clean”) and those with one and two next neighbour carbons, labeled “p(2x2)” and “c(2x2)” respectively.
unaffected by carbon atoms further away. This reduction of apparent height is approximately 20 pm for metal atoms with one nearest neighbour carbon (e.g. in the p(2 × 2) structure) and 40 pm with two carbon nearest neighbours (c(2 × 2) structure). This change of apparent height cannot be explained by geometry, as the existence of the adsorbate rather leads to an outward shift of the first substrate monolayer [5]. Other reasons for this change of apparent height may be a reduction of local density of states (LDOS) or some kind of tip-surface interaction. Since we have observed a decrease of apparent height with very different tunneling conditions and different tips, we do not attribute it to a special tip-sample interaction mechanism. In view of theoretical predictions, a reduction of the LDOS seems more plausible. Calculations based on the assumption of four carbons neighbouring a Ni atom [21–23] predict a very slight reduction of the LDOS at the Fermi level for Ni atoms only, while a recent study [24] finds a more pronounced reduction in the c(2 × 2) structure (two nearest neighbour carbons). Furthermore, it was shown that next nearest neighbour carbon atoms have no influence on the density of states [21–23]. Although these results are in agreement with our STM observations, we should note that at the low tunneling resistance used for figs. 1 and 2 the apparent height does not depend on the density of states alone but more complicated tip-sample interactions may play a role.

Fig. 2, which is more typical of STM images of this surface, also shows regions of different apparent height; the height differences are somewhat larger than in fig. 1: from their symmetry (blocks of 2 × 2 atoms, e.g. at the right end of the section), we can identify the p(2 × 2) regions, which are about 40 pm below the highest metal atoms (i.e., those without carbon neighbours, not counting the shifted rows, which are still slightly higher). As in fig. 1, we also find many atoms at the p(2 × 2) height level which do not exhibit this symmetry, nevertheless they have one C nearest neighbour. The darker regions are approximately 70 pm below the carbon-free areas, comparing their size and shape with fig. 1 shows that the metal atoms in these areas must have two nearest neighbour carbons, i.e. local c(2 × 2) structure. These height values are found with very sharp tips only (note the good resolution near the step edge at the lower terrace in fig. 2); with average tips typical values are −20 pm and −40 pm for the p(2 × 2) and c(2 × 2) height levels, respectively, in good accordance to the apparent height reduction in fig. 1.

Since the shifted rows do not show these brightness variations and fig. 1 does not show any indications of C atoms neighbouring these rows, we conclude that these sites are unfavourable for carbon. The reason for this effect is not clear, it may be either geometrical or due to a high Pt concentration in the shifted rows. Unfortunately, no chemically resolved STM images distinguish-
ing between Pt and Ni [20], which would help us deciding this question, have been obtained on this surface yet.

Compared to the substrate distortion on Ni(100) derived from LEED [4,5], we have found no or very weak substrate distortion in the areas of c(2 × 2) carbon coverage of most STM images, such as figs. 1 and 2. Only after multiple cycles of oxygen admission and substrate heating, followed by Ar sputtering (removing most of the oxygen) and heating, we have detected a pronounced case of this distortion, shown in fig. 3. The maximum lateral shift of the metal atoms in this image is approximately 50 pm, in good agreement with 45 ± 7 pm derived from LEED [5].

One possible reason why the substrate distortion is weak or totally invisible in most other images might be tip–sample interaction lifting the distortion. While most images have been taken at very low tunneling distances (tunneling resistance in the order of 100 kΩ), causing strong tip–sample interaction, fig. 3 was obtained at much larger tunneling resistance (350 MΩ). This means that the tip–sample distance was larger and therefore the sample was under less influence of the tip. However, the existence of areas with different amounts of substrate distortion in fig. 3 cannot be explained by the assumption of tip–sample interaction lifting the distortion; we therefore reject this assumption.

Nevertheless, the absence of visible substrate distortion in most other STM images does not necessarily imply that the substrate is undistorted there, it seems rather plausible that the distortion is invisible due to thermal vibrations, causing a rapid flipping of the metal atoms between the two equivalent positions of the distorted structure (similar to the apparently symmetric dimers on Si(100) [25]). In such a case the substrate distortion is not detectable by STM unless it is pinned somewhere. In fig. 3, this pinning may be due to impurities (possibly oxygen remaining from the oxidation treatment). These impurities may also explain the cloudy appearance of some parts of the image.

We conclude that we have found many similarities between the structure of carbon on the Pt_{10}Ni_{90}(100) surface studied by STM and the respective surface of pure nickel. Carbon leads to a reduction of the apparent height of the neighbouring metal atoms, probably caused by a deduced density of states at the Fermi level shown in previous calculations. Individual carbon atoms can be directly seen under special tip conditions only, indicating some kind of chemical interaction between the imaging tip atom and the carbon atom. A strong substrate distortion known from earlier LEED measurements of Ni(100) was directly imaged on the Pt_{10}Ni_{90}(100) surface only once. The absence of visible substrate distortion in the other images is tentatively attributed to a rapidly moving atom arrangement, which may be pinned at impurities.

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References


