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## Scanning tunnelling microscopy studies of Pt<sub>80</sub>Fe<sub>20</sub>(110)

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**Abstract.** Results of scanning tunnelling microscopy (STM) show that two different kinds of surface structures coexist on the (110) surface of Pt<sub>80</sub>Fe<sub>20</sub>. The predominant structure corresponds well to the missing row type (1×2) reconstruction previously observed on, for example Pt(110), whereas the minority domains show a faintly buckled structure with approximately (1×1) geometry. Based on the STM images, we propose that the two domains have different surface chemical compositions and correspond to two different metallurgical phases known for the PtFe system at this composition.

The (110) surfaces of the 5d transition metals Ir, Pt and Au have been extensively discussed in the literature. They have all been reported to possess (1×2) and (1×3) reconstructions, and large efforts on both the experimental and the theoretical side have been made to deduce the local geometry of these superstructures. In the case of Pt and Au, a missing row model, in which the surface decomposes into (111) microfacets through the removal of every second close-packed row, is now generally accepted. Observations of these surfaces have been reported in a number of scanning tunnelling microscopy (STM) studies [1, 2, 3]. Ir, on the other hand, was recently found to have an entirely different (110) surface, showing a rippled structure with (331) facettings on a mesoscopic scale [4].

The enhanced catalytic properties, as compared to pure Pt, of some binary alloys between Pt and 3d metals have motivated detailed investigations of their surface regions concerning both segregation and atomic geometry. In a recent low-energy electron diffraction (LEED) study [5], (1×2) and (1×3) reconstructions were also observed for the (110) surface of Pt<sub>80</sub>Fe<sub>20</sub>. The (1×2) reconstruction was found to have an atomic configuration very close to the case of pure Pt(110) [6]. The main difference seemed to be larger interlayer distances in the surface region, e.g. 13 instead of 20% contraction in the first layer, but the general trend is very similar and the authors concluded that the origins of the (1×2) reconstructions are probably the same [5]. However, the agreement between the experimental and the theoretical  $I/V$ -curves was rather poor as compared to other surfaces, and a surface structure analysis on the more local scale, as provided by STM, seems well motivated.

In this paper we report findings from STM measurements on the same sample as were used in [5]. Of greatest significance is the observation of two types of well defined surface

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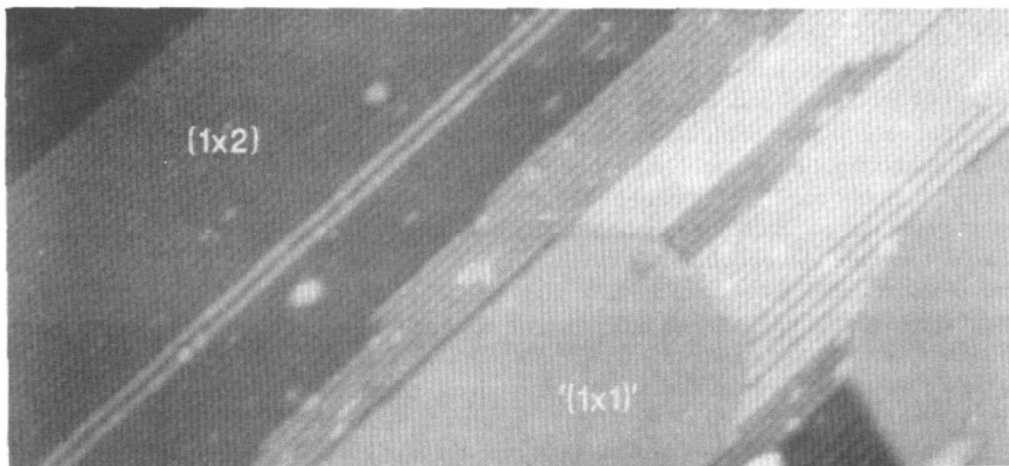
domains. One is recognized to have the same missing row type ( $1 \times 2$ ) reconstruction as previously has been observed on, for example, Pt(110) [2, 3], whereas the other, which has no counterpart in the case of the pure metal, shows a slightly distorted ( $1 \times 1$ ) structure. Based on the STM images, metallurgical data for the PtFe system, and considerations for the surface segregation, we propose that these domains have different surface chemical compositions, and suggest that they correspond to two different metallurgical phases expected from the bulk phase diagram to coexist in the crystal at this composition. In addition, we note that the STM results presented here, e.g., the presence of two coexisting surface structures, may in part explain the moderate agreement in the LEED study [5].

The STM [7] is housed in an ultra-high-vacuum (UHV) system, with a base pressure in the low  $10^{-10}$  Torr range, also containing a sample preparation/analysis chamber including LEED, electron bombardment sample heating and sputtering facilities. The sample consists of a Czochralski grown  $\text{Pt}_{80}\text{Fe}_{20}$  single crystal with a carefully aligned and mirror polished (110) surface. The Pt content was controlled by x-ray fluorescence measurements to be  $80 \pm 0.5$  at.%. According to the bulk phase diagram [8] this composition corresponds to a two-phase region, extending from 78.5 to 82.8 at.% Pt, between an ordered  $\text{Cu}_3\text{Au}$ -like structure (denoted  $\gamma_3$ ) and a disordered solid solution ( $\gamma$ ). It has previously been shown [5] that the present crystal is mainly in the ordered state, but with possible occurrence of  $\gamma$ -phase parts. The lattice parameter was determined with x-ray diffraction analysis to  $3.89 \pm 0.01$  Å, in reasonable agreement with previously published values [8].

In vacuum the sample was cleaned by means of repeated cycles of  $\text{Ar}^+$  ion sputtering and annealings, a procedure which previously has been shown to produce a clean surface on the present sample as analysed by Auger electron spectroscopy (AES) [5]. In the final stage, the sample was annealed to 900 °C and a LEED pattern corresponding to the ( $1 \times 2$ ) phase, as described in [5], was obtained. Some very faint features indicated the presence of small ( $1 \times 3$ ) reconstructed areas. The STM images, which were acquired with electrochemically etched W tips, showed large flat areas with a low density of resolved impurities.

Figure 1 displays a representative overview image of the surface. The ribbon-like structure is similar to what previously has been observed on Pt(110) [2, 3] and corresponds to the ( $1 \times 2$ ) and, to a much less extent, ( $1 \times 3$ ) reconstructions. The corrugation amplitudes in the [001] direction, i.e., orthogonal to the rows, were measured to be about 0.5 and 1.5 Å respectively, which is close to the values reported for Pt [3]. In general, no atomic resolution was obtained along the rows. In agreement with the observations on Pt(110) [3] the step density and the amount of disorder were found to be much larger in the [001] direction than in the  $[1\bar{1}0]$  direction. This explains the streaky character of the LEED pattern in the [001] direction which has been observed for this surface, and which was discussed in [5]. More interesting is the presence of the flatter regions seen in the middle and right parts of figure 1. Such regions, which were readily found after each sputtering/annealing cycle, were often well aligned with the ( $1 \times 2$ ) and ( $1 \times 3$ ) reconstructed areas, and seemed to, as a rough estimate, occupy about 20% of the surface. Figure 2, a partial magnification of figure 1 in which the contrast has been enhanced using a differential smoothing routine [9], shows that these regions have a distorted ( $1 \times 1$ ) surface structure. We will refer to this structure as ' $1 \times 1$ ' throughout this paper, emphasizing the close relationship with a true ( $1 \times 1$ ) geometry, regarding the areal density of surface atoms, for example, but also indicating the distortion. The corrugation of the atomic rows in the [001] direction is  $\approx 0.05$  Å, whereas no atomic resolution was found in the close-packed  $[1\bar{1}0]$  direction.

Two interesting features can be recognized for these ' $1 \times 1$ ' areas. First, the distortion, which is due to a two-dimensional sine-wave-like buckling of approximately 0.1 Å in amplitude, seen as the faint pattern within these domains in figure 1. These buckling patterns



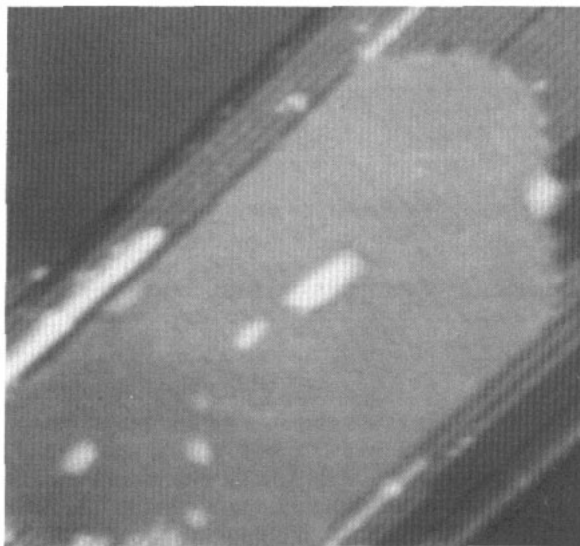
**Figure 1.** An  $850 \times 385 \text{ \AA}^2$  STM image of the  $\text{Pt}_{80}\text{Fe}_{20}(110)$  surface acquired at 10 mV sample to tip voltage and with a tunnelling current of 1 nA. The locations of the different surface regions are indicated. In addition, small areas with a  $(1 \times 3)$  structure can be seen.



**Figure 2.** An enlarged section from figure 1, showing the  $(1 \times 1)$  structure. The contrast has been enhanced using a differential smoothing routine, but this has also reduced the magnitude, and hence visibility, of the buckling.

are not perfectly identical between the domains. The related periodicities and directions of propagation are essentially the same, but there are slight deviations, presumably connected to the domain geometries. In figure 2 for instance, where only the shorter periodicity is visible due to the smoothing routine, the pattern is very close to parallel with the  $[001]$  direction. This is not a general trend, but is probably a consequence of the upper domain boundary being parallel with the  $[001]$  direction. This effect, the alignment with the domain boundaries, can clearly be recognized by a comparison of the two domains in figure 1. Furthermore, the buckling patterns are not constant within the domains, but slight and continuous changes are frequently observed, and the presence of impurities is sometimes found to cause more abrupt changes. An example of the latter can be seen in figure 3. Second, as measured from an average plane within the buckling, the  $(1 \times 1)$  domains appears  $0.40 \pm 0.1 \text{ \AA}$  higher than the  $(1 \times 2)$  areas, which suggests a difference in surface

relaxation. This height difference may be due partly to an electronic effect, e.g. in part it merely reflects the doubled atomic density in the '(1×1)' top layer. In order to obtain the true geometric step height, it would be necessary to determine this electronic contribution. As a rough estimate, this can be done using the atomic charge density superposition method described by Tersoff and Hamann [10]. Adopting the workfunction  $\phi = 5.3$  eV [11] from the case of pure platinum for both structures, and fitting calculated contours to the measured corrugation of the (1×2) structure, a simulated electronic height difference of 0.11 Å between the '(1×1)' and (1×2) areas is hereby obtained. The reliability of this exact value can of course be questioned, but it is fairly insensitive to the parameters—at least if these are chosen within the range of physical plausibility—and it can be taken to provide a reasonable estimate of the real magnitude. The assumption of equal workfunctions may seem critical, and a possible difference would certainly affect the result to some extent. However, since the more smooth and close-packed '(1×1)' structure can be assumed to have a higher workfunction [12], this would rather give a correction in the opposite direction, i.e. a lower apparent height of the '(1×1)' structure. However, for small differences in workfunction (<1 eV), this correction is not crucial (<0.03 Å). We also note here that the (1×2) and (1×3) structures are approximately equal in height.



**Figure 3.** A  $410 \times 380$  Å<sup>2</sup> STM image of a contaminated (presumably with carbon) '(1×1)' domain, showing a distorted buckling pattern.

Based on the above arguments, the geometric step height between the '(1×1)' and (1×2) domains can in a first approximation be estimated to exceed 0.20 Å. As the first interlayer distance in the (1×2) structure was found to have a contraction of  $\simeq 13\%$  as compared to the bulk [9], this implies that the '(1×1)' areas rather have a slight expansion in the top-layer spacing. This is also supported by the STM images in two other respects. First, the presence of the buckling in the '(1×1)' domains indicates strong repulsive interaction between the surface atoms. No corresponding buckling has been found in the (1×2) domains. Second, the domain boundaries between the '(1×1)' and (1×2) areas do show signs of the expected strain due to the difference in surface relaxation. The in-plane boundaries are either separated by trenches corresponding to a monatomic step or show some kind of local disorder.

The similar atomic arrangements of the (1×2) structures of Pt<sub>80</sub>Fe<sub>20</sub>(110) and Pt(110) [5, 6] motivates a comparison with theoretical models and calculations for the pure metal.

Following the discussion of Heine and Marks [13] on the atomic forces at noble metal surfaces, Fery, Moritz and Wolf [6] suggested that the contraction in the top-layer spacing of  $Pt(11)(1 \times 2)$  is related to a redistribution of the electron density from the repulsive d bands to the attractive sp bands in the surface region. This kind of argument may also be applicable to the  $Pt_{80}Fe_{20}$  surface, provided that the chemical composition in the surface is essentially the same as in the bulk. However, for  $Pt(110)$ , the same argument would also hold for a  $(1 \times 1)$  reconstruction. In fact, theoretical calculations using the embedded atom method [14] and the LCAO formalism [15] predict an even stronger contraction in this case. This is obviously in contrast to what is observed on  $Pt_{80}Fe_{20}$ . A possible explanation is that the surface chemical composition differs between the ' $(1 \times 1)$ ' and  $(1 \times 2)$  domains, with a higher platinum content in the ' $(1 \times 1)$ ' regions. The bulk lattice parameter is  $\approx 3.89 \text{ \AA}$  as compared to  $3.924 \text{ \AA}$  for pure platinum, and a possible deviation from the bulk composition in the surface would induce strain effects. For instance, would surface enrichment of platinum give rise to an expansive pressure, and possibly buckling and expansion phenomena like those observed in the ' $(1 \times 1)$ ' domains?

The surface segregation for a number of dilute binary alloys of transition metals have been treated theoretically by Miedema [16]. In the case of Fe in Pt, a surface enrichment of platinum was predicted. This also had some support from an AES study, in which it was concluded that iron does not segregate to the surface of polycrystalline Pt ( $\sim 2\%$  Fe) [17]. In the case of single-crystalline  $Pt_{80}Fe_{20}$ , which differs from the dilute case in having mainly an ordered bulk structure, both the (110) and the (111) surfaces have been examined by means of quantitative LEED analysis [5, 18]. The results indicated platinum segregation for the close-packed surface, whereas the (110) surface was found to have essentially the bulk composition.

We now suggest that the different surface domains are related to the different metallurgical phases of the sample. The disordered  $\gamma$ -phase has a slightly larger platinum content and corresponds to a somewhat larger lattice parameter [8]. Furthermore, since it can be assumed to have more pronounced surface segregation effects [19], a correspondence to the ' $(1 \times 1)$ ' domains seems likely. The  $(1 \times 2)$  domains, on the other hand, show no sign of lateral stress, indicating a more bulk-like surface composition as would be expected from the ordered  $\gamma_3$ -phase. These ideas are further supported by the fact that they relate the dominant surface structure to the majority phase of the bulk.

It is not totally surprising that an introduction of excess surface strain would include a  $(1 \times 2) \rightarrow (1 \times 1)$  structural transformation. These structures have been calculated to have very close total energies for the clean Pt and Au (110) surfaces [14, 15, 20]. However, no large  $(1 \times 1)$  domains with any similarities to those here observed on  $Pt_{80}Fe_{20}$  have been reported for these surfaces [1-3].

It seems likely that the presence of two different surface domains has influenced the LEED investigation in [5]. We suggest that they are partly responsible for the moderate agreement, another contribution being the lack of order in the [001] direction as mentioned above. Yet, it seems that the STM results support the outcome of these LEED calculations to some extent. The step height between the ' $(1 \times 1)$ ' and  $(1 \times 2)$  structures is consistent with a contraction of the topmost spacing in the  $(1 \times 2)$  domains, and the absence of buckling or any sign of lateral stress in the  $(1 \times 2)$  domains agrees well with a bulk-like composition at the surface.

In summary, we have studied the (110) surface of  $Pt_{80}Fe_{20}$  by means of STM under UHV conditions. Two different kinds of surface domains have been observed. One has mainly a  $(1 \times 2)$  reconstruction, with small insets of a  $(1 \times 3)$  structure, which is consistent with the missing row model previously suggested for this surface. The other domain type

has a buckled ( $1 \times 1$ ) structure which appears somewhat higher than the ( $1 \times 2$ ) and ( $1 \times 3$ ) reconstructions. The characteristics of the domains lead us to suggest that they correspond to two different metallurgical phases, known to coexist in the alloy at this composition. We believe that this work further emphasizes the importance of combining averaging techniques like LEED, with more local probes such as STM, and suggest that the presence of the ' $1 \times 1$ ' areas can partly explain the moderate agreement in the previous LEED study of this sample.

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