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STM/TEM comparative study of Pd clusters epitaxially grown on highly oriented pyrolytic graphite

S. Granjeaud(1), K. Yckache(1), M. Dayez(1), A. Humbert(1), C. Chapon(2) and C.R. Henry(2)

(1) GPEC - URA CNRS 783, Campus de Luminy, Case 901, 13288 Marseille Cedex 9, France
(2) CRMC2 - CNRS, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France

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Résumé. — Des agrégats de Pd de taille de 1 à 100 nm sont déposés à haute température sur du graphite HOPG et observés par microscopie par effet tunnel (STM) et par microscopie électronique en transmission (TEM). Ces deux techniques donnent des informations complémentaires. La morphologie des particules est facilement observable par STM à toutes tailles, tandis qu'elle est seulement obtenue en TEM pour les grosses particules. Les informations cristallographiques (structure cristalline, orientation des facettes, épitaxie) peuvent être obtenues, sur des particules individuelles par TEM si leur taille est supérieure à 5 nm. La structure de surface des agrégats ne peut être atteinte que par STM. Le microscope par effet tunnel est également mieux adapté pour visualiser les très petits agrégats.

Abstract. — Pd clusters in the size range 1-100 nm are grown at high temperature on HOPG and observed by STM and TEM. These two techniques give complementary information. The morphology of the particles is easily obtained by STM at all sizes, while TEM is limited to the observation of larger clusters. Crystallographic informations (internal structure, facet orientation, epitaxy) can be obtained on individual particles by TEM, but only if the particles are larger than about 5 nm. However the surface structure of clusters is only attainable by STM. STM is also more efficient to detect very small clusters (<1.5 nm).

1. Introduction.

Supported clusters are generally characterized *ex-situ* by transmission electron microscopy (TEM) [1]. Recently scanning tunneling microscopy (STM) has been used to study such systems [2-12], mainly on graphite supports. However few works combine TEM and STM observations on the same samples. Although STM has become a powerful tool for surface analysis and is able to give insight in the topography of metal clusters deposited on surfaces, it is necessary to have some references to calibrate this new technique.

In this paper we present a comparison, on the same samples, of TEM and STM studies on palladium clusters deposited at high temperature on highly oriented pyrolytic graphite (HOPG). We have focused this work on the size distribution, topography and shape of the clusters.

2. Experimental.

HOPG supports were cleaved in air and cleaned in-situ by annealing at 500 °C during 5 hours under ultra high vacuum (UHV). The graphite substrate was kept at 320 °C during deposition obtained by condensing a calibrated atomic beam of Pd atoms ($6 \times 10^{13} cm^{-2}.s^{-1}$ during 4 minutes). After deposition, the samples are transferred, through air, in the STM chamber where they are imaged, in the constant current mode, at 1×10^{-7} Torr. After STM observations, graphite flakes transparent to the electron beam of TEM (obtained by peeling) are observed in a Jeol 2000 FX electron microscope. Several micrographs from different areas of the sample are taken. Size distributions of the clusters from TEM micrographs are obtained by using a manual size analyzer. STM images are analyzed by an interactive computing method.

3. Results.

3.1 TOPOLOGY OF THE DEPOSIT. — Figure 1 represents a TEM micrograph of an area of 42 μm^2 on the sample. We can see a very high linear density ($1.5 - 2 \times 10^5 cm^{-1}$) of aligned clusters with sizes of 20 to 30 nm. Theses clusters are located along atomic steps of the graphite surface and decorate these linear defects. Between steps the clusters are very large (60 to 90 nm), but have a very weak surface density ($4.5 \times 10^7 cm^{-2}$). A careful observation of figure 1 shows that most of the clusters on the terrace have nucleated on visible surface defects. Figure 2 shows a particular decoration pattern characterized by a high density of small clusters ($3 \times 10^{11} cm^{-2}$) with a size range 2 to 4 nm, surrounded by large particles (20 to 40 nm). These features result certainly from cluster nucleation and growth on structural point defects or impurities [13-14].

Figure 3 is a size histogram obtained from TEM observations and representative of the whole sample (the total analysed area was 255 μm^2). It exhibits mainly two large peaks. The first one, approximately centred at 21 nm corresponds to clusters on steps. The second one at about 70 nm is representative of large isolated clusters between steps. If the shape of clusters is known, the condensation coefficient of Pd on HOPG can be determined; it is estimated to be between 1 and 2%. This very low condensation coefficient is characteristic of high temperature growth on a clean graphite surface containing few defects [13-14].

Figure 4 represents a large scale and high resolution STM image showing mainly small Pd clusters in the size range 1 to 4 nm. Some particles have a well defined triangular outline. As will be seen in the next paragraph, these particles have a tetrahedral shape. Besides these small clusters we have also observed by STM some large clusters. The size distribution of the Pd particles observed by STM is shown in figure 5. On the same figure, the TEM size distribution is also represented. This figure shows clearly that most (≈90%) of the clusters imaged by STM have a size around 2 nm. The remaining clusters (≈10%) are distributed in a broad peak between 20 and 40 nm. They correspond to clusters decorating steps and give rise to the main peak in the TEM size distribution. The very large clusters (70-90 nm) observed by TEM have not been studied by STM.

3.2 CLUSTER SHAPES. — The high magnification TEM micrograph of the figure 6 shows Pd clusters on a step and three isolated large clusters on the flat graphite surface. These clusters

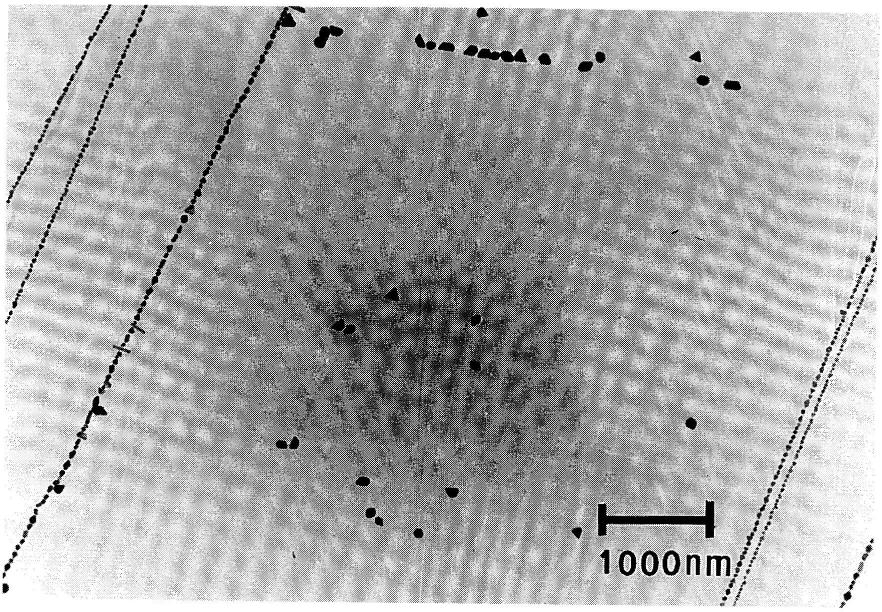

Fig. 1. — Low magnification TEM micrograph of a high temperature Pd deposit on graphite.

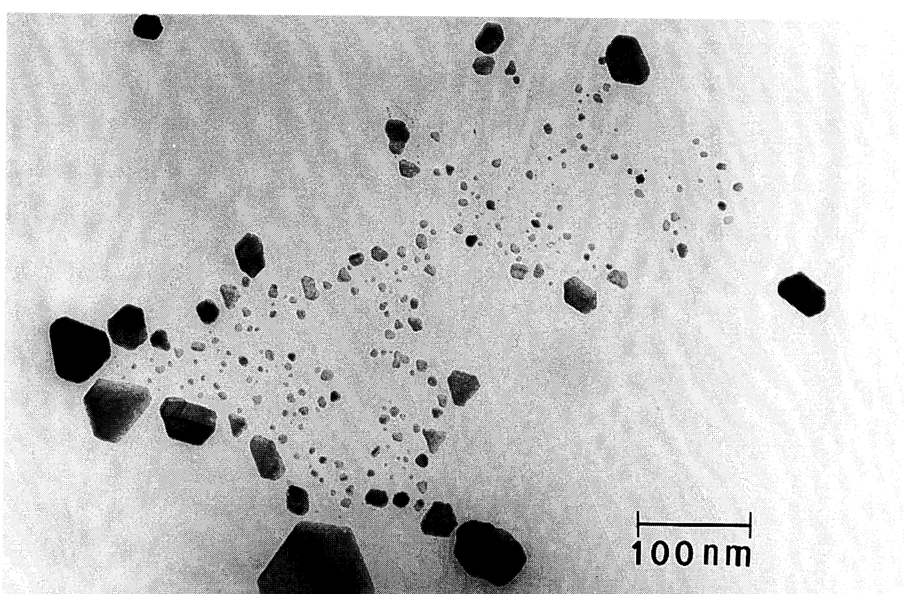

Fig. 2. — TEM micrograph of a defect area on a graphite surface decorated by Pd clusters.

present a contrast from their edges and then it is possible, knowing the crystallographic orientation of the basal plane and lateral facets, to determine the height/diameter ratio (h/d). With the chosen

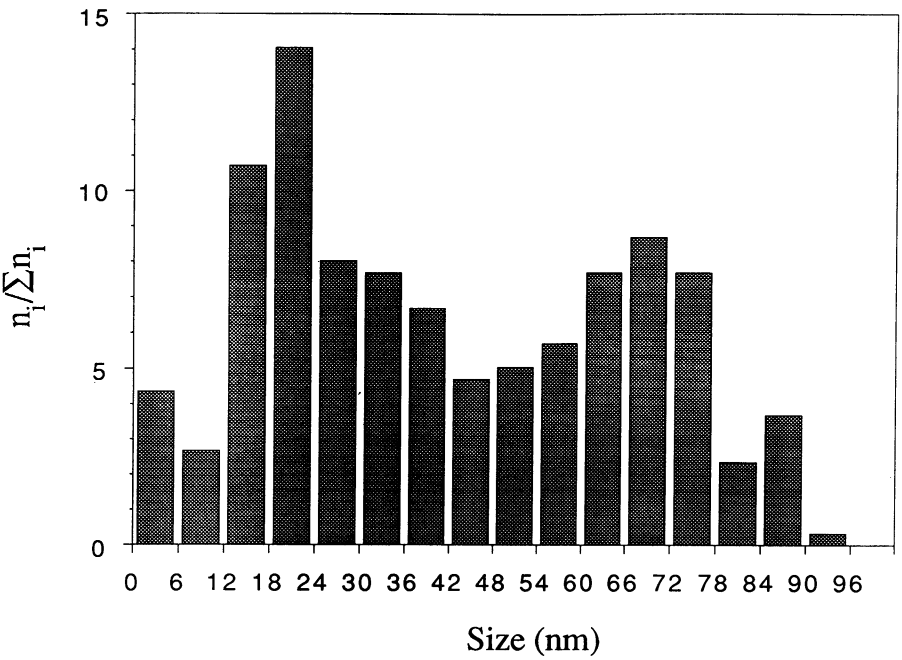

Fig. 3. — Size histogram of Pd particles deduced from TEM micrographs representative for the whole sample.

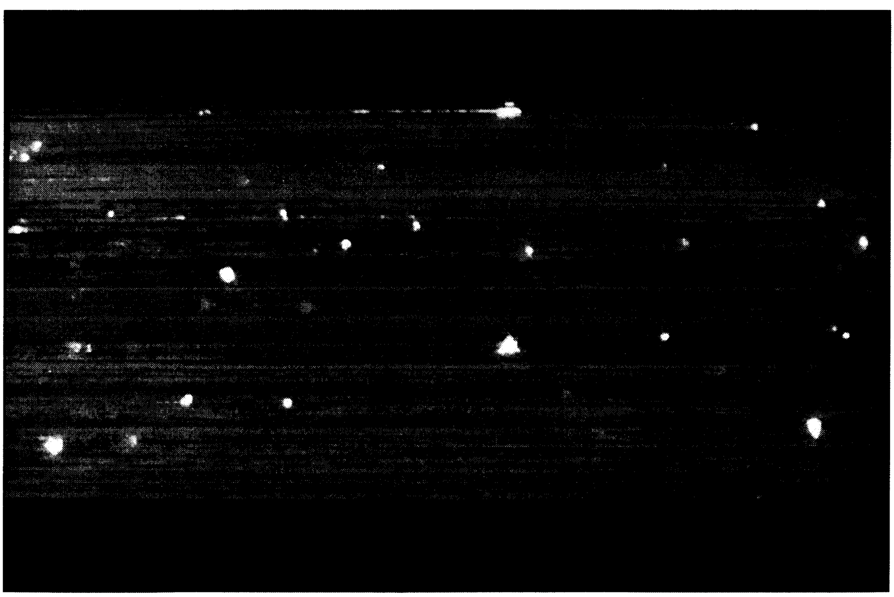

Fig. 4. — STM image (112.2 × 51.5 nm^2) of small Pd clusters on HOPG.

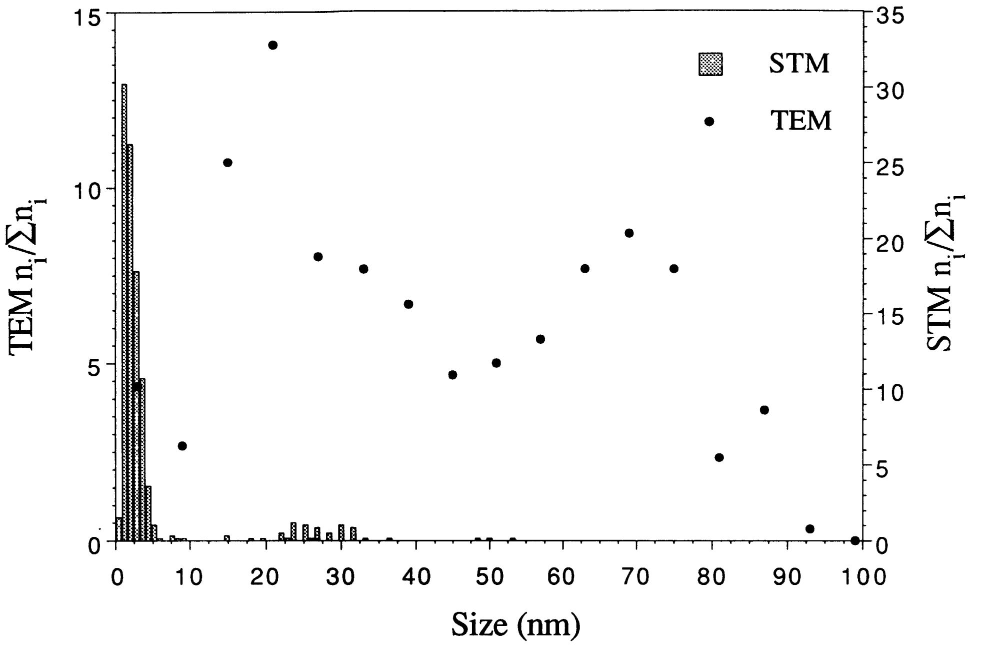

Fig. 5. — Comparison of STM (bars) and TEM (points) size histograms from the same Pd/HOPG sample.

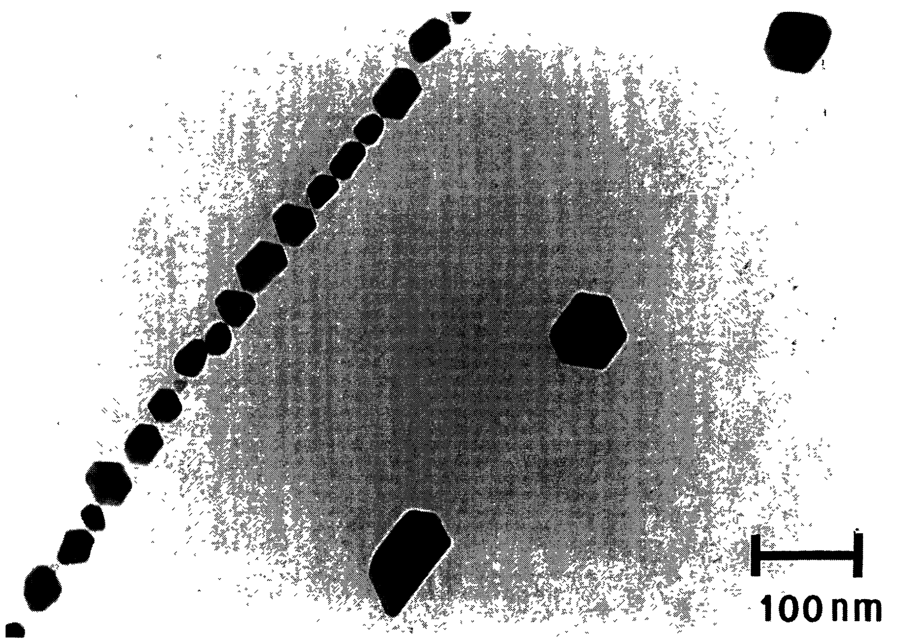

Fig. 6. — High magnification TEM micrograph of Pd particles on a step and on a flat area.

experimental conditions, clusters are growing in (111) epitaxy on the graphite [7]. The most likely facets for high temperature growth of Pd are (111) and (100) [15]. Pd clusters along the step, have the well defined shape of a truncated tetrahedron and a mean ratio $h/d = 0.3 - 0.4$, while the pseudo-hexagonal cluster on the terrace has a h/d ratio of 0.12. Contrasts from the crystallite edges are seen in TEM only on clusters larger than 20 nm.

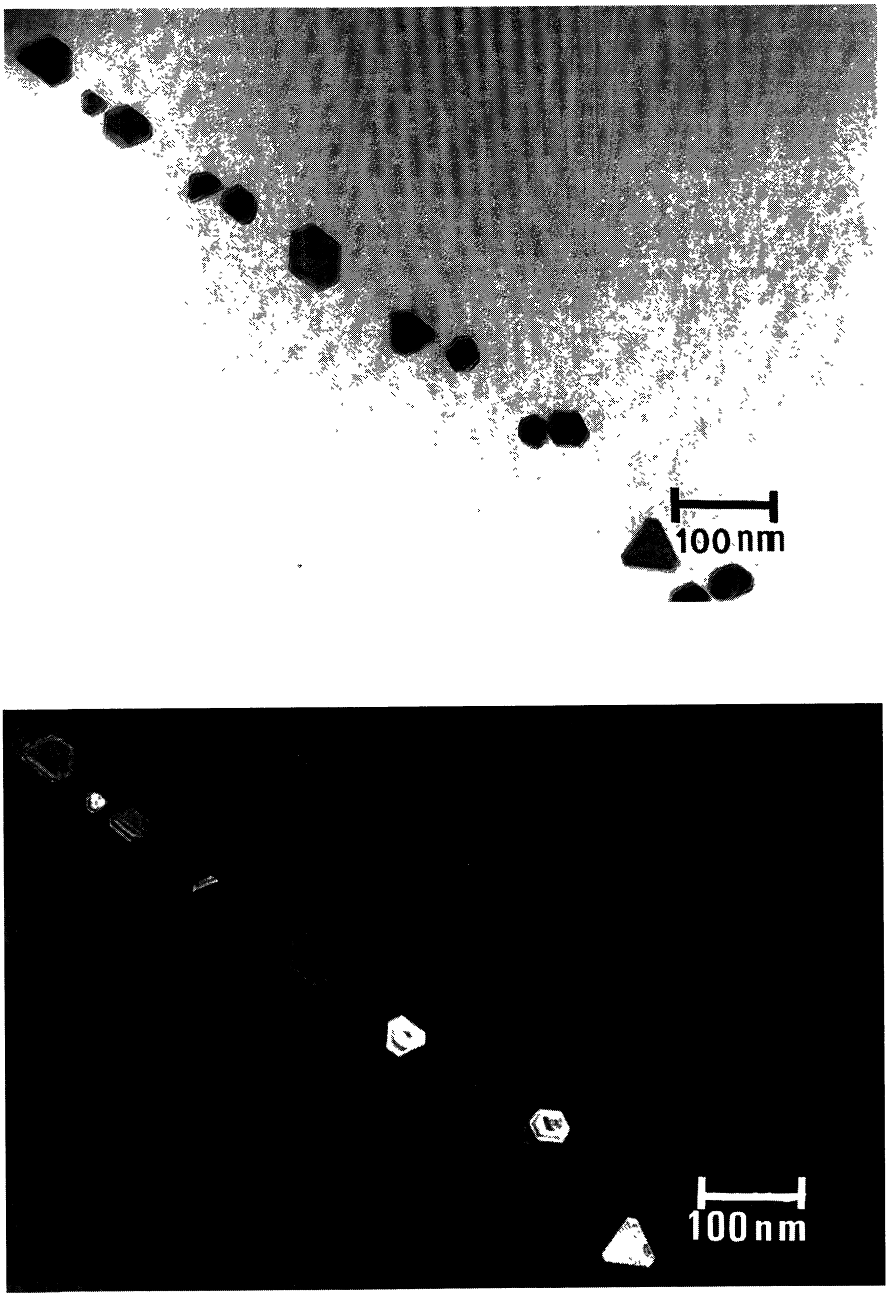

Fig. 7. — Bright Field (a-top) and Weak Beam Dark Field (b-bottom) images pair of Pd particles along a graphite step.

For smaller crystallites another quantitative method can be used: the weak beam dark field technique (WBDF) [16]. This method uses the dynamical effect of the electron beam - crystal interaction. In practice, an image from a single reflection is taken after tilting the sample a few degrees from the Bragg condition. We observe thickness fringes with a spacing depending on the facet orientation. This method can only be applied for particles larger than 5 nm. Figure 7 presents a pair of bright field and WBDF images from clusters in a step. We see clearly that the extension of the lateral facets is not the same for the different particles. Roughly the h/d ratio increases from 0.07 to 0.65 as the cluster size decreases. The fine fringes on the triangular particle of figure 7b are Moiré fringes due to a small rotation of the particle lattice relatively to the substrate.

Figure 8 shows a STM image of a 60 nm pseudo hexagonal particle. From STM we measure directly a h/d ratio of 0.07 in very good agreement with TEM measurement.

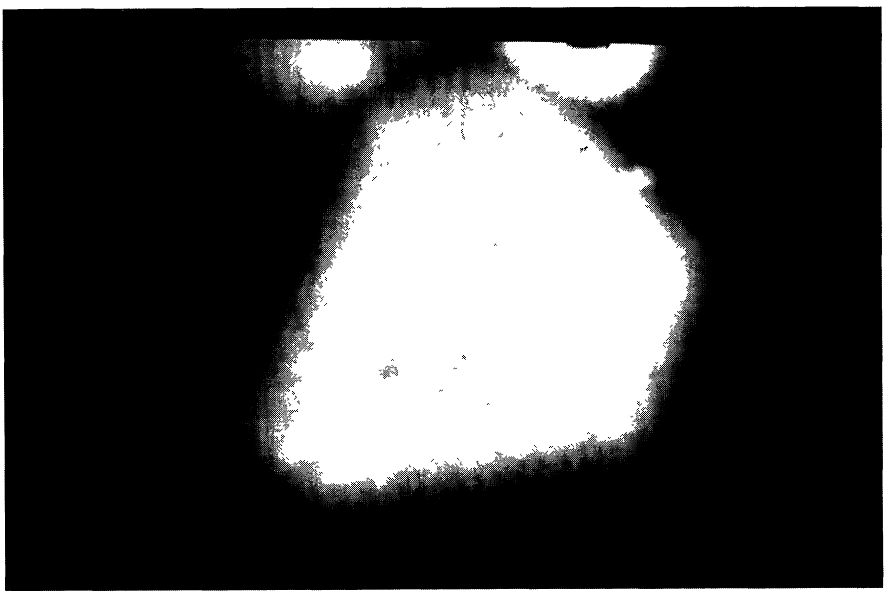

Fig. 8. — STM image (103.8 × 74.1 nm^2) of a large pseudo hexagonal Pd cluster on HOPG.

Figure 9, extracted from STM data of figure 4, shows a 1.5 nm tetrahedral particle. Only STM is able to resolve the three dimensional shape of such small particles.

3.3 CLEAVAGE DEFECTS. — Generally cleavage produces atomic and some macroscopic steps. In addition, other peculiar features are seen on graphite. Figure 10 shows such a feature revealed by TEM. Steps of different heights are decorated by Pd clusters. The figure is interpreted as follows: a band of graphite of width 160 nm has been raised up during cleavage and folded. Figure 11 shows such a macroscopic defect observed by STM. The rectangular flake of 90 nm in width, on the bottom of the figure has been raised up and twisted by an angle of 20°.

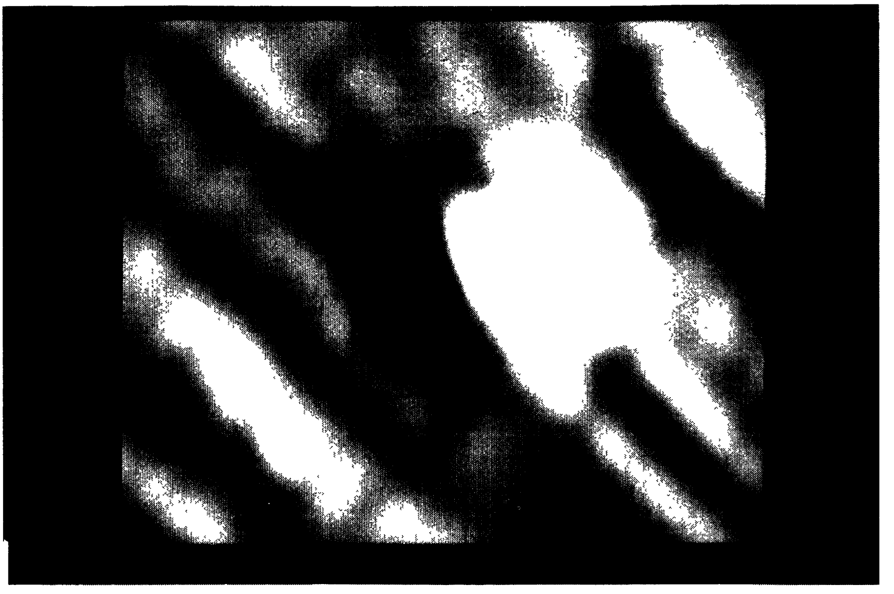

Fig. 9. — STM image (3.6×3.0 nm^2) of a tetrahedral Pd particle.

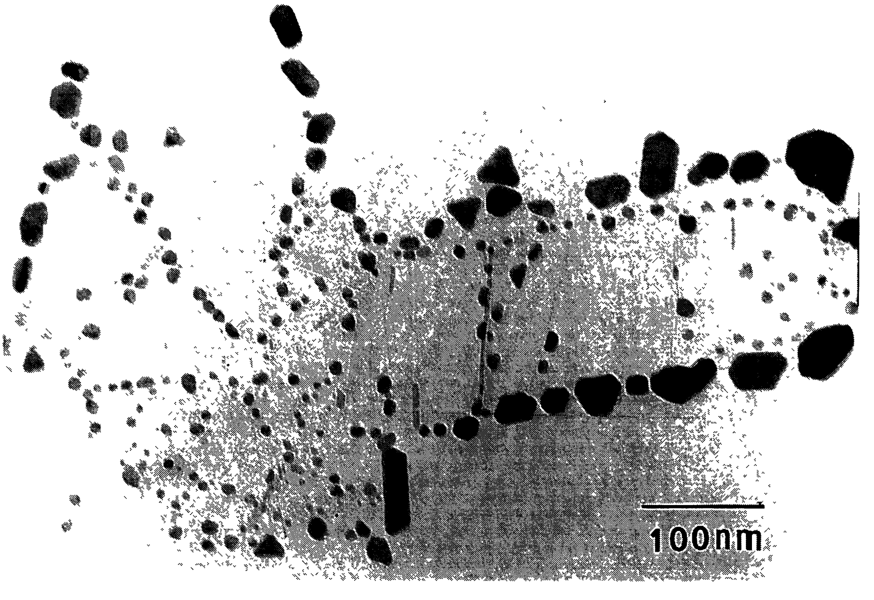

Fig. 10. — TEM micrograph of a cleavage defect on graphite decorated by Pd clusters.

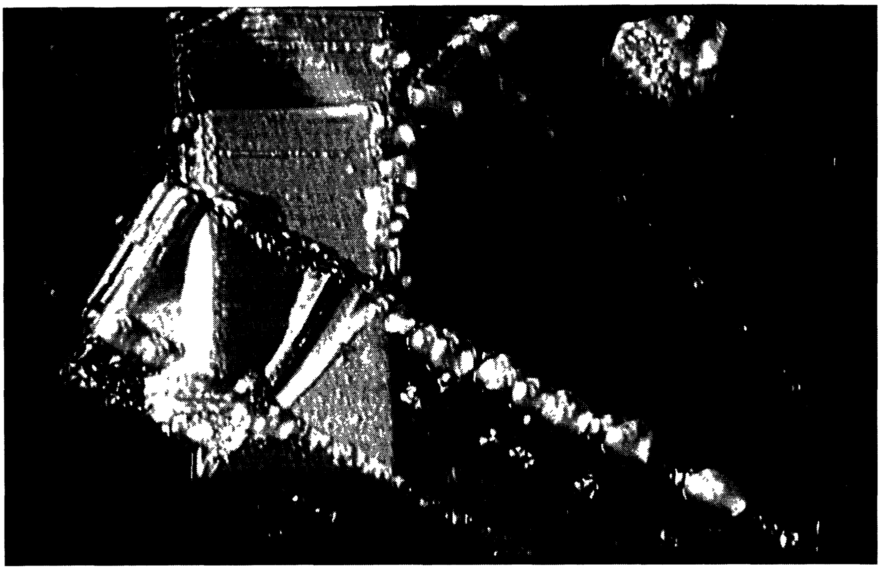

Fig. 11. — STM image (491 × 340 nm^2) of a cleavage defect decorated by Pd.

4. Discussion.

This TEM-STM study of Pd clusters on graphite allows one to compare the advantages and the limitations of the two techniques. TEM is more efficient for the study of large clusters (>20 nm) and information on a great number of particles is easy to obtain. However conventional TEM operates ex-situ and samples must be thinned. This can result in restructuring by oxidation in air and damage or loss of some particles. Particles smaller than 1.5 nm can be detected by TEM, but their shape cannot be obtained. STM can be used for the whole size range of particles. The three dimensional shape can be reached in all cases but we need a calibration in the case of metallic particles on a foreign substrate. In the present STM study, the statistical analysis of the data looks poorer than those generally obtained by TEM, mainly because of the small size of the chosen STM window. This is not an intrinsic limitation of STM. An advantage of STM is its ability to work in UHV. However we have to be aware of some artefacts in STM images which are due to a possible interaction between the tip and the sample. In this case, the tip can move small aggregates on the sample during the scan. Also the shape observed by STM is a convolution of the actual shape of the particles with the form of the STM tip. This is mostly true for clusters much higher than about 1 nm (tunneling gap). Nevertheless comparison of STM and TEM observations on a same sample is satisfactory.

The clusters in the medium size range (10-50 nm) are observed by both techniques and their size distributions are comparable, taking into account for the weak number of counted particles (about 500 in each case). However the proportion of these particles is very different in the two size distributions. This difference is mainly due to the much greater number of very small particles observed in STM. The cluster shape revealed by the two techniques is also in good agreement. The two techniques show that as the particles increase in size they flatten. The smallest particles have a tetrahedral shape. In previous STM studies in air, we showed that their facets had an atomic arrangement corresponding to (111) planes [7]. We believe that it is the shape of the smallest stable nucleus (4 atoms). Later on, the clusters grow preserving this shape up to a size of at least 2 nm. Then, the clusters flatten by truncation of their top and on edges by (111) and (100) facets.

In conclusion, combination of STM and TEM observations is revealing for the study of supported clusters because these two techniques give complementary information.

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