

# Bimetallic PdCu and PdCu<sub>3</sub> Particles Prepared by Wet Impregnation-HRTEM Study of the Structure and the Interface with the MgO Substrate

Suzanne Giorgio and Claude Henry

CRMC2 (\*), CNRS, Campus de Luminy Case 913, 13288 Marseille Cedex 9, France

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**Abstract.** — Bimetallic particles of PdCu and PdCu<sub>3</sub> are prepared by decomposition of organometallic compounds on MgO micro-cubes. During the annealing between 350 and 400 °C, in reducing atmosphere, PdCu particles grow with the fcc structure, without defined shape. The particles epitaxially (001) oriented on MgO are dilated and accommodated to the substrate. After annealing at 450 °C, the particles adopt the  $\beta$  ordered structure. The particles are limited at the edges by (100) and (110) faces. Most of them are oriented (001) on MgO with [110]PdCu || [100]MgO, which corresponds to a perfect accommodation of the lattices without deformation compared to the bulk, despite of the reduction in H<sub>2</sub>. The PdCu<sub>3</sub> particles smaller than about 10 nm were found with the  $\alpha$  ordered structure, without periodic anti-phase boundaries.

## 1. Introduction

Pd is used as catalyst for CO oxidation [1] and hydrogenation of butadiene, it is not efficient for the reduction of NO. Alloying Pd with Cu, enhances the selectivity in the hydrogenation of dienes [2,3] and the activity for the reduction of NO by CO [4,5]. The increasing rate of the catalytic reactions is associated to considerations on structural/electronic properties, surface segregations, alloying effects and metal-substrate interactions.

According to the phase diagram of the bulk alloy, Pd and Cu form a continuous solid solution of fcc structure, with two ordered phases ( $\beta$ PdCu with the CsCl structure and  $\alpha$ PdCu<sub>3</sub> with the AuCu<sub>3</sub> structure). The  $\beta$  and  $\alpha$  phases are stable below 598 °C and 508 °C respectively [6].

In the  $\alpha$  structure, long period superstructures have been observed with periodic anti phase boundaries. The variations in the periodicity was studied by high resolution electron microscopy as a function of composition and temperature of annealing [7].

Surface segregation on the different crystallographic orientations have been studied by various surface science techniques [8]. *In situ* HRTEM has been also used to determine the chemical nature of the surfaces of  $\beta$ PdCu particles, during annealing in CO [9]. Pd segregation was found

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(\*) Laboratoire associé aux Universités d'Aix-Marseille 2 et 3.

on the (100) faces. In PdCu clusters prepared by wet impregnation of silica, Low Energy Ion Scattering (LEIS), showed surface segregation of Cu presumably at the low coordination sites, edges and corners according to Monte-Carlo simulations [3].

Other calculations also predict Cu segregation on PdCu bimetallic clusters [10–12].

Pd<sub>50</sub>Cu<sub>50</sub> colloids particles prepared at 135 °C showed the disordered fcc phase [13], while Pd<sub>50</sub>Cu<sub>50</sub> particles prepared by decomposition of acetylacetonate precursors at 400 °C [3] or 500 °C [14], have the ordered  $\beta$  structure. PdCu particles grown under UHV by condensing Pd and Cu atoms on a NaCl (100) surface at 350 °C have the fcc structure. After annealing at 400 °C under UHV they get the  $\beta$  structure [15,16].

LEIS has also shown a copper enrichment with the composition (Pd<sub>45</sub>Cu<sub>55</sub>) on the (111) surface of a Pd<sub>50</sub>Cu<sub>50</sub> bulk single crystal [4]. In the case of the (110) surface, a pure Cu surface was observed [17].

Polycrystalline PdCu alloy films also show a slight surface enrichment in copper [18].

Here, Pd<sub>50</sub>Cu<sub>50</sub> and PdCu<sub>3</sub> clusters have been prepared by the decomposition of organometallic precursors (acetylacetonates) on clean MgO micro-cubes previously annealed in air at 900 °C.

We describe the morphology, the internal and interface structure of the Pd<sub>50</sub>Cu<sub>50</sub> clusters supported on MgO, after annealing under H<sub>2</sub>, in the temperature range 350–500 °C.

In the case of PdCu<sub>3</sub>, after annealing at 500 °C during 5 days in reducing atmosphere, we obtained the ordered phase  $\alpha$ PdCu<sub>3</sub>. without antiphase boundaries for sizes below 10–20 nm.

## 2. Preparation

The preparation of the Pd-Cu particles by decomposition of acetylacetonate (acac) on MgO powder (10 m<sup>2</sup> g<sup>-1</sup>) has been previously described [16]. Here, after the filtration of the precipitate, the powder is dried and slowly annealed until 350 °C in vacuum, then at increasing temperatures in reducing atmosphere of H<sub>2</sub>. For the preparations of Pd<sub>50</sub>Cu<sub>50</sub> clusters, a proportion of  $1.28 \times 10^{-2}$  mole of Pd(acac)<sub>2</sub> and  $0.505 \times 10^{-2}$  mole of Cu(acac)<sub>2</sub> per gram of MgO was taken.

For PdCu<sub>3</sub> particles, these proportions were  $1.20 \times 10^{-2}$  mole of Pd(acac)<sub>2</sub> and  $1.42 \times 10^{-2}$  mole of Cu(acac)<sub>2</sub> per gram of MgO.

Both samples were annealed under H<sub>2</sub> (400 Torr). Pd<sub>50</sub>Cu<sub>50</sub> clusters were annealed for 3 hours at 350, 400, 450 and 500 °C. PdCu<sub>3</sub> particles were annealed for 3 hours, then 5 days at 500 °C. Before the observation in electron microscopy, the samples were coated *ex situ* with a thin carbon film.

For diffraction studies, some macroscopic single crystals of MgO (6 mm × 6 mm) were added to the mixture, filtered and annealed with the powders, then covered with carbon. The carbon replica containing the PdCu particles were observed by electron microscopy.

## 3. HRTEM Observations of Pd<sub>50</sub>Cu<sub>50</sub> Clusters

The samples were observed with a Jeol 2000FX electron microscope for the X-ray fluorescence analysis and a Jeol FEG 2010 microscope for the high resolution studies.

Equivalent compositions of 50% atoms of each metal were determined at the level of the isolated clusters by X-ray fluorescence in the electron microscope.

Particles annealed at 350 °C have the fcc structure. The diffraction pattern of the carbon replica contains spots and rings (Fig. 1) with the (200) and (111) reflections of PdCu (fcc). Some of them, among the smallest (2–3 nm diameter) are in the (001) epitaxial orientation

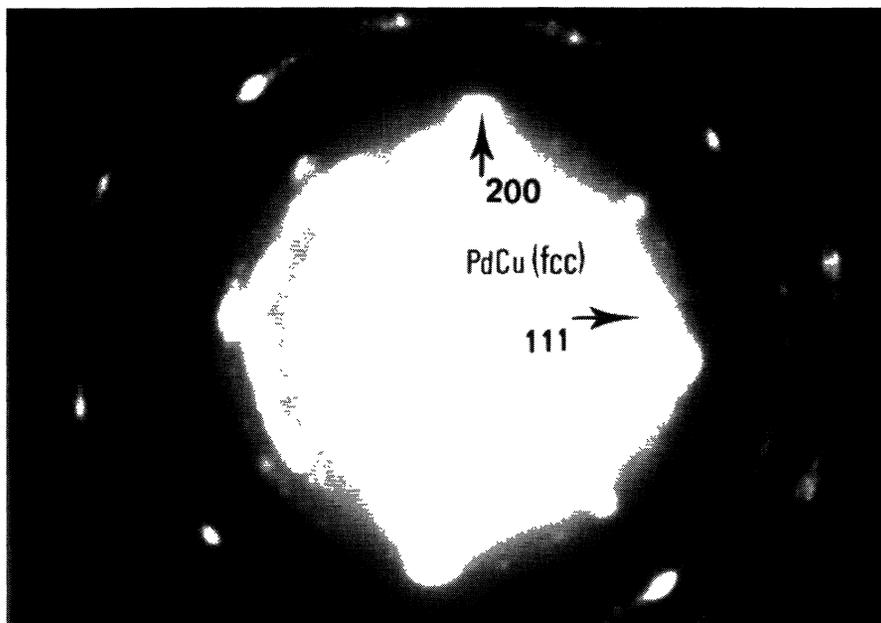


Fig. 1. — Diffraction pattern of a replica with particles annealed at 350 °C under H<sub>2</sub>.

on MgO, a few in the (110) orientation, and others show a large disorder or a random orientations can be seen. Figure 2 is the HRTEM image of a MgO micro-cube with two particles in the (110) orientation and in the middle, one particle in the (001) orientation. The shapes are undefined. As in the case of pure Pd particles prepared under UHV [19] or by decomposition of organometallics compounds on clean MgO cubes [14], the PdCu particles which are epitaxially oriented (001) from the HRTEM images of top and profile views, are accommodated to the substrate at the level of the first layers at the interface.

After annealing at 400 °C, the diffraction pattern of the carbon replica supporting PdCu particles, contains rings (Fig. 3) corresponding to the (100) and (110) reflections of  $\beta$ PdCu and weak (200) reflections of fccPdCu. The HRTEM images, again show a large distribution of orientations. The major part of the particles have no regular shape.

After annealing at 450 °C, the particles have only the (100) orientation. The high resolution images of all the particles in top view and cross-sections correspond to the  $\beta$  ordered structure. The particle size varies between 4 and 8 nm. Compared to the particles obtained at 350 °C, the size increase is due to coalescence during annealing at higher temperature. Figure 4a shows several PdCu particles in top view and in cross-section. The thickness of the MgO substrate corresponds to the side of the cube (16.8 nm). A 4 nm sized particle is seen in top view on MgO. The outline shape is a polygon, limited by 4 sides in the [100] directions and 4 less extended sides in the [110] directions. For this half octahedral shape, the particle thickness is directly deduced from the basis. The lattice of metal is epitaxially oriented on the substrate according to the relations: (001)PdCu || (001)MgO and [110]PdCu || [100]MgO. At the centre of the particle, the contrast of the image allows the recognition of the metal atoms positions, by comparison with the simulations near the Scherzer focus, which was necessary to get a different contrast between Pd and Cu. All the simulations were performed by using the EMS program (from P. Stadelman [20]) and the supercells were constructed with the program "Epitax"

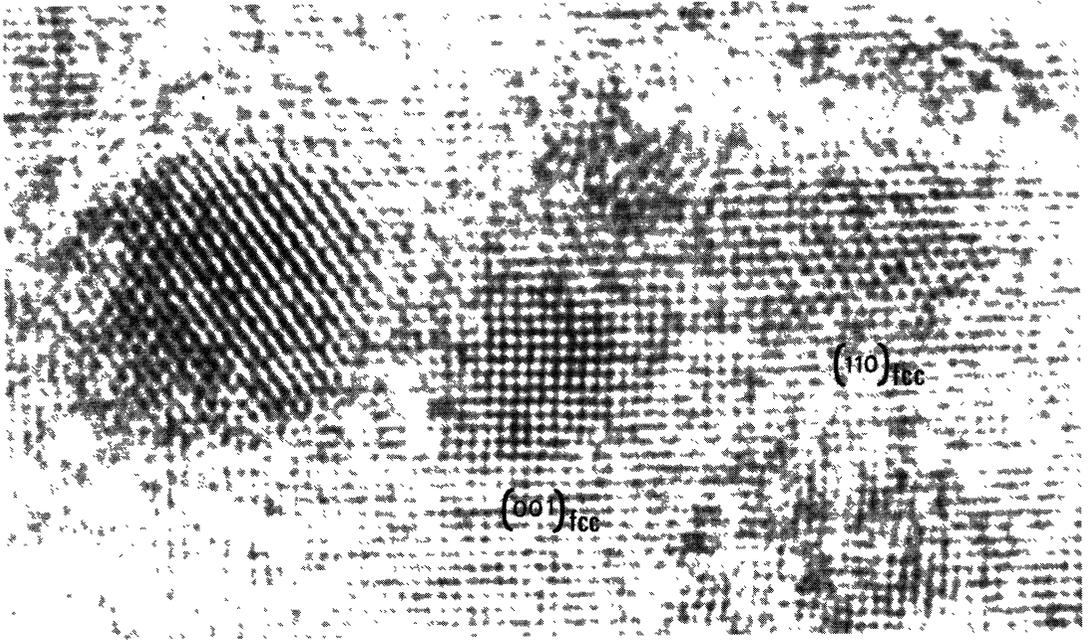


Fig. 2. — HRTEM image of PdCu (fcc) particles (2-4 nm) oriented (001) and (110) on MgO.

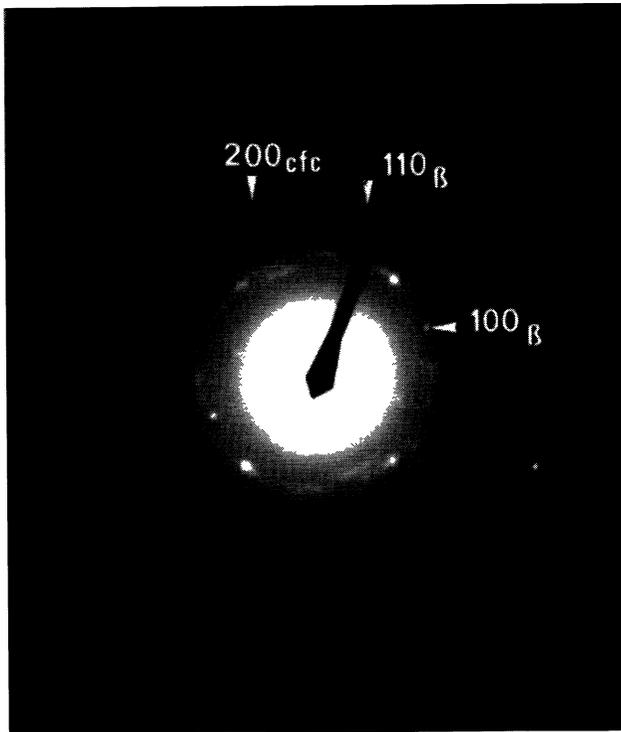


Fig. 3. — Diffraction pattern of a replica with particles annealed at 400 °C under  $H_2$ .

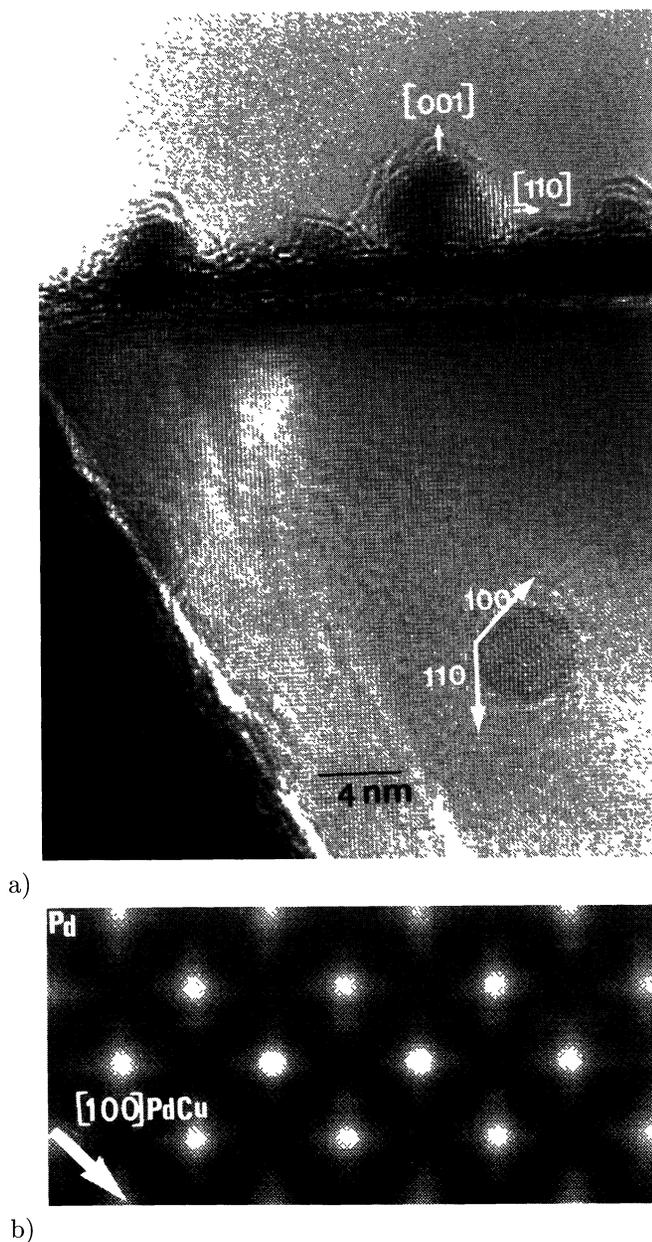
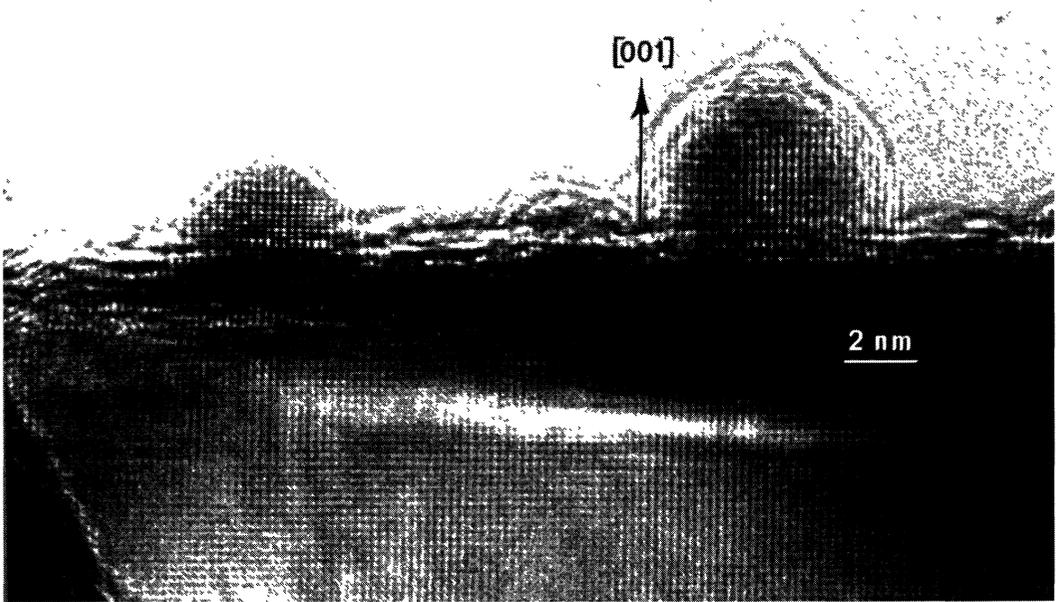
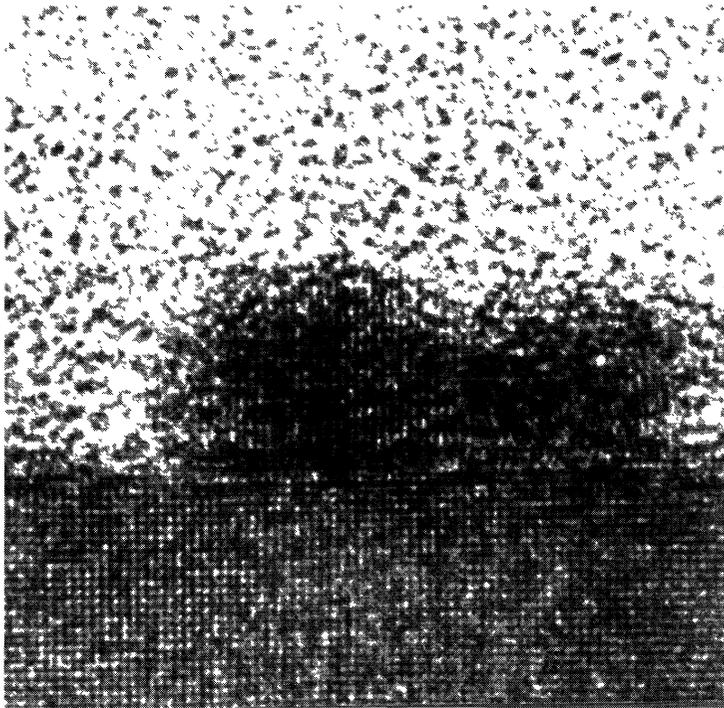


Fig. 4. — (a) Top and profile view of PdCu particles ( $\geq 4$  nm) on MgO (001) (MgO thickness = 65 nm). (b) Simulated image of PdCu[100] (thickness = 2.9 nm), superimposed with MgO (thickness 16.8 nm) at the Scherzer focus. (c) Profile views of the same particles as in Figure 4a at the Scherzer focus at the level of the particles. (d) Profile view of a particle at the top of a MgO cube. Scherzer focus at the level of the particle and the surface of MgO. (e) Simulated image of PdCu in [110] orientation, thickness 4.2 nm. The origin at the bottom left is a Pd atom. The grey spots in the dark fringes are Cu atoms.



c)



d)

Fig. 4. — Continued.

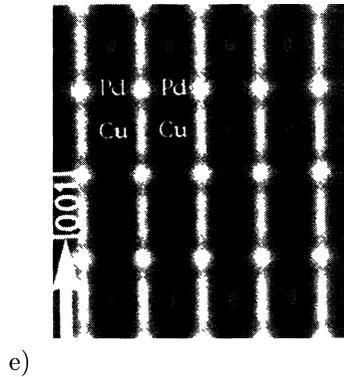


Fig. 4. — Continued.

(from S. Hagege, [EPITAX v2.5]). In Figure 4b, the PdCu lattice (thickness 3 nm) is superimposed to the MgO lattice (16.8 nm) with a Pd atom at the origin. The superimposition of both lattices does not invert the contrast in PdCu. The contrast of the image corresponds to the Pd or Cu metal atoms aligned with the atomic columns of MgO.

In the profile views of Figure 4a, for the epitaxial orientation described above, the particles in cross-section are seen along a  $[110]$  direction. The largest particle on the right side has been imaged at the Scherzer focus (Fig. 4c). Both particles are limited by  $[001]$  directions at the edges perpendicular to the interface and at the top. The truncations at the edges are more pronounced than at the top.

According to the MgO thickness and the position of the particle on the edge of MgO, it is possible to image the PdCu/MgO interface in more detail. The dark fringes in the metal are aligned with the dark fringes of MgO (see Fig. 4d).

The dark fringes in the metal, perpendicular to the interface, correspond to the positions of Pd or Cu atoms, as seen in the simulated images of PdCu in the  $(110)$  orientation (Fig. 4e) for a thickness of 4.2 nm. In the simulations of the PdCu/MgO interface, with a layer of Pd or a layer of Cu at the interface in Figures 5a and 5b respectively, the contrast between both Pd and Cu atoms is attenuated compared to the bulk PdCu.

The simulations in profile view, for the same thickness, were also performed in the case of the metal atoms in bridge positions between the Mg and O ions (Fig. 5c). There, the dark fringes in the metal are shifted by half a period compared to those of MgO.

All the images in Figures 5 were simulated at a defocus of 43 nm which minimizes the Fresnel fringe at the interface. The good agreement between the experimental and the simulated images is consistent with the alignment of PdCu rows with the atomic columns of MgO.

The lattice distance between the  $(110)$  planes normal to the interface was measured in the PdCu particles. The intensity profiles were recorded as described in reference [19], along the  $[110]$  directions of the PdCu particles parallel to the interface. The MgO lattice was taken as an internal calibration, with a sampling of 1 pixel for 0.008 nm at the level of the sample.

We can see in Figure 5d that the PdCu lattice is nearly accommodated to the substrate with the bulk value of the  $\beta$  structure of the alloy ( $a = 0.29$  nm). The lattice of the Pd particles prepared by the same technique [14] was always found with a dilatation of at least 4% in the volume, due to the reduction in  $H_2$  and a dilatation of 8% at the interface for a perfect accommodation with the substrate. Here, we observe almost a perfect coincidence between the lattices of PdCu  $(001)$  oriented on MgO  $(001)$  with  $[110]PdCu \parallel [100]MgO$ . According to the

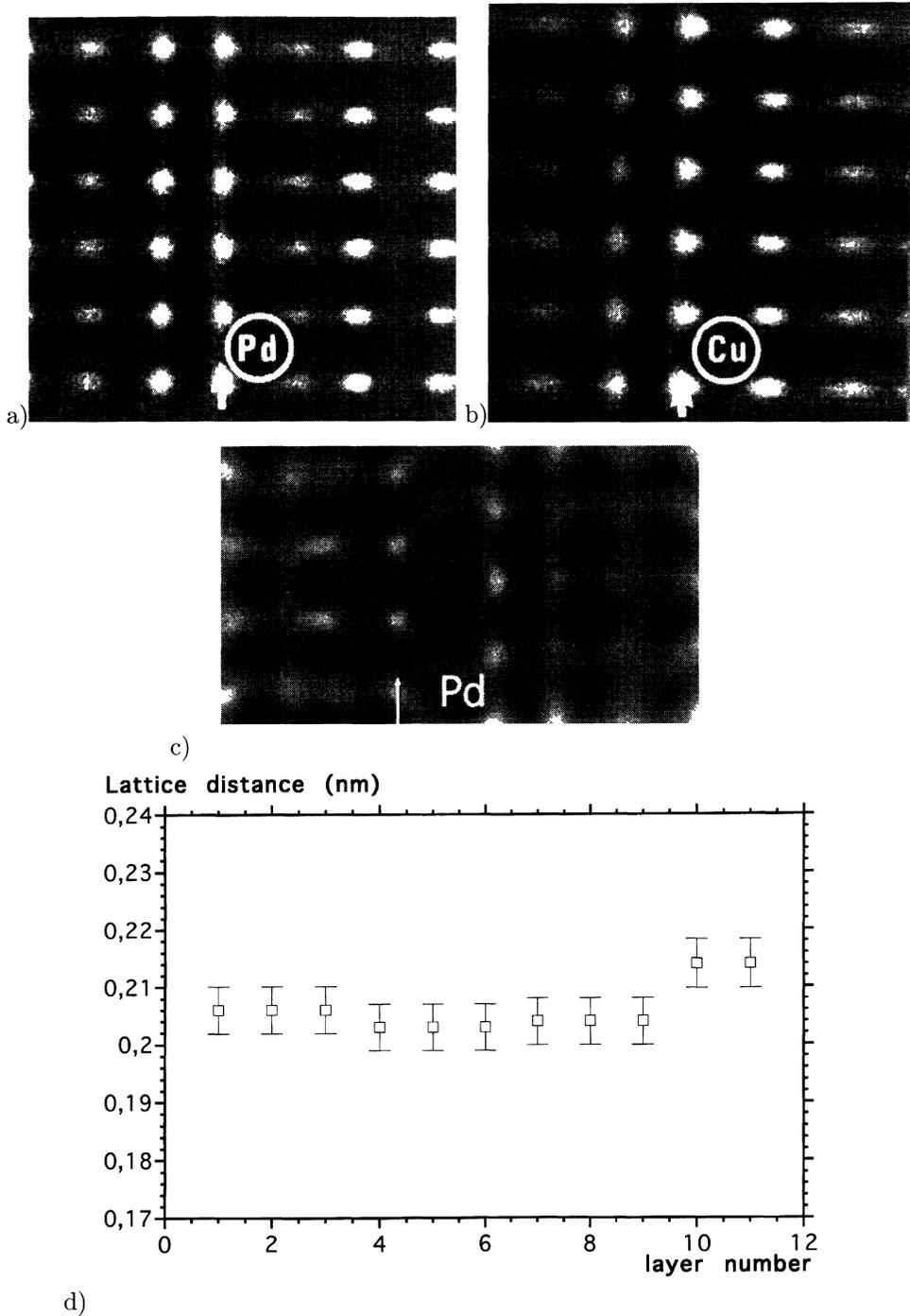


Fig. 5. — (a) Simulated image of PdCu(110) on MgO(001), with atoms of Pd at the interface in front of the column of MgO, thickness 4.2 nm. The arrow indicates the interface line. The position of a Pd atom is marked. The atomic columns of MgO appear as dark fringes. (b) Simulated image of PdCu(110) on MgO(001), with atoms of Cu at the interface in front of the column of MgO, thickness 4.2 nm. (c) Simulated image of PdCu(110) on MgO(001), with atoms of Pd at the interface, located in bridge position between the Mg or O ions. (d) Lattice distance between the (110) planes in PdCu, from the interface to the top.

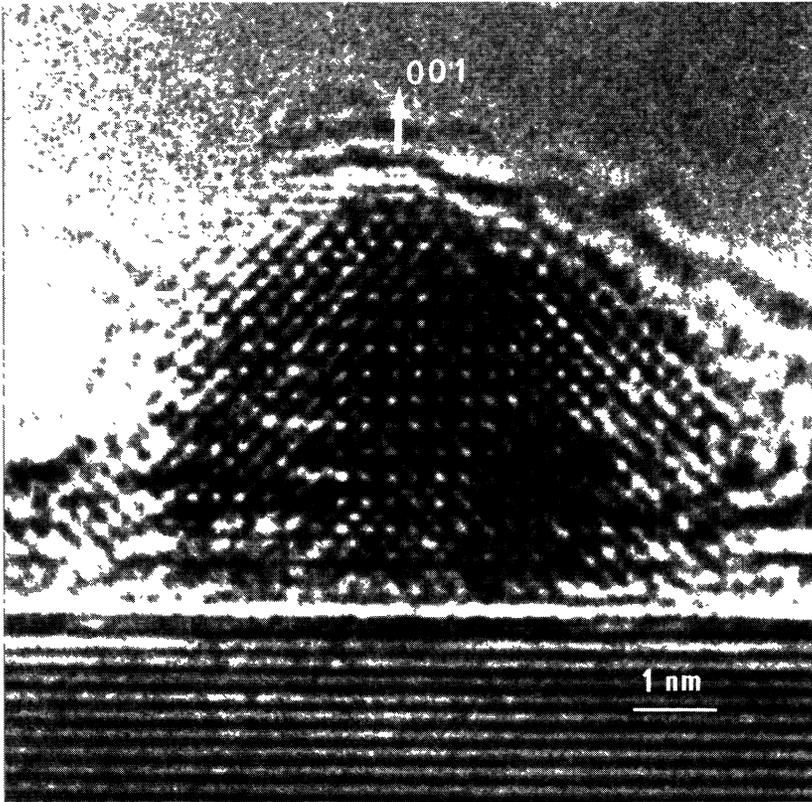


Fig. 6. — Profile view of a PdCu particle on MgO(110).

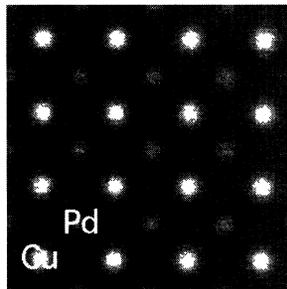


Fig. 7. — Simulated image of PdCu in the [100] orientation, (thickness 7.5 nm), the origin at the bottom left is a Pd atom (in grey), the Cu atoms are bright.

measurements, the PdCu lattice is even contracted by about 1% compared to the bulk value.

For the (110) orientation of the MgO cube, the particles are seen along the [001] direction. From the comparison between Figure 6 and the simulated image for 8 nm thickness (Fig. 7), the atomic columns of Pd and Cu can be identified in the particle. The Fresnel fringe does not allow to deduce directly the composition of the interface and according to the simulations, the contrast between Pd and Cu is attenuated near the interface, in the 5 first layers.

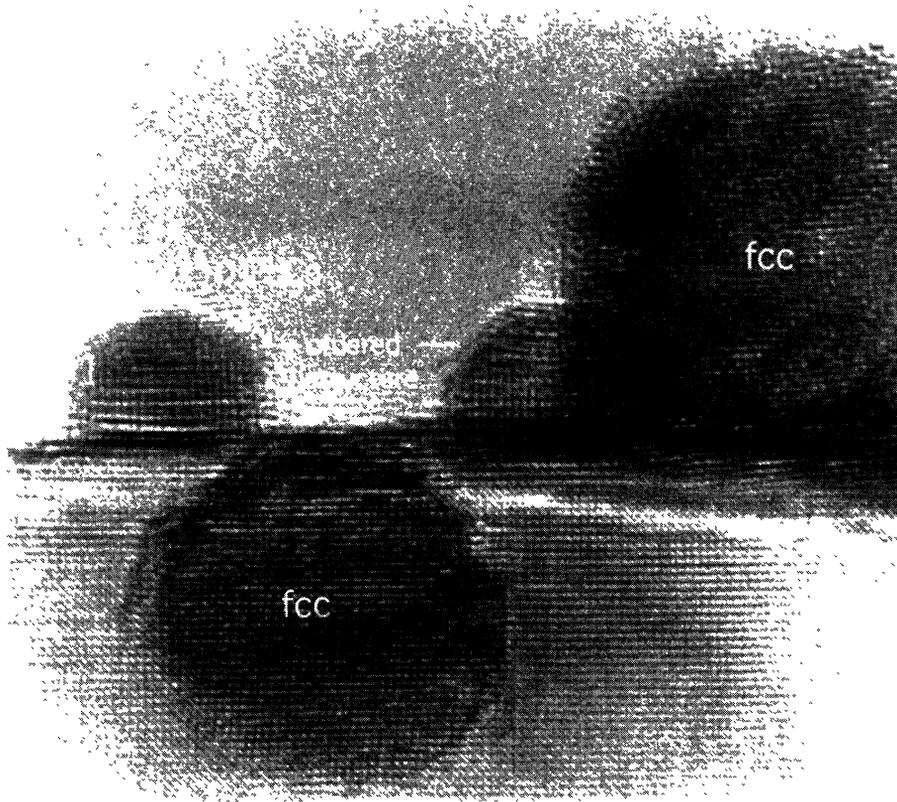


Fig. 8. — HRTEM image of 2 small PdCu particles with the ordered  $\beta$  structure and 2 large particles with the fcc structure.

Some PdCu particles with a larger size ( $> 10$  nm) were obtained by using higher concentrations of acac in solution. Figure 8 shows 4 particles, 2 small ones (4-5 nm), with the ordered  $\beta$  structure at the left side and two large ones, in top and profile view which are fcc and more or less rotated with respect to the substrate. It shows that after annealing at 500 °C during 24 hours, the larger particles are still fcc, which is out of equilibrium from the phase diagram, and certainly due to a kinetic barrier.

#### 4. HRTEM Observations of PdCu<sub>3</sub> Particles

Compositions of 75% ( $\pm 2\%$ ) Cu atoms and 25% ( $\pm 2\%$ ) Pd atoms were determined by X-ray fluorescence in the microscope.

Particles (9-20 nm) annealed under H<sub>2</sub> at 500 °C for 3 hours have no regular shapes and random orientations. The ordered  $\alpha$  AuCu<sub>3</sub> structure is found, with defects and twins.

After annealing at 500 °C for 5 days, the shapes are cap-shaped with a ratio of the height over the diameter of about 0.6. Most particles are in epitaxy with two main orientations: (001) and (110) on MgO (001). In Figure 9a, a particle ( $\sim 7$  nm) is seen in top view with (001) orientation on MgO (001) with  $[100]\text{PdCu}_3 \parallel [110]\text{MgO}$ .

Figure 9b represents a 9 nm particle (110) oriented on MgO in top view. Some stacking faults are visible on the left side.

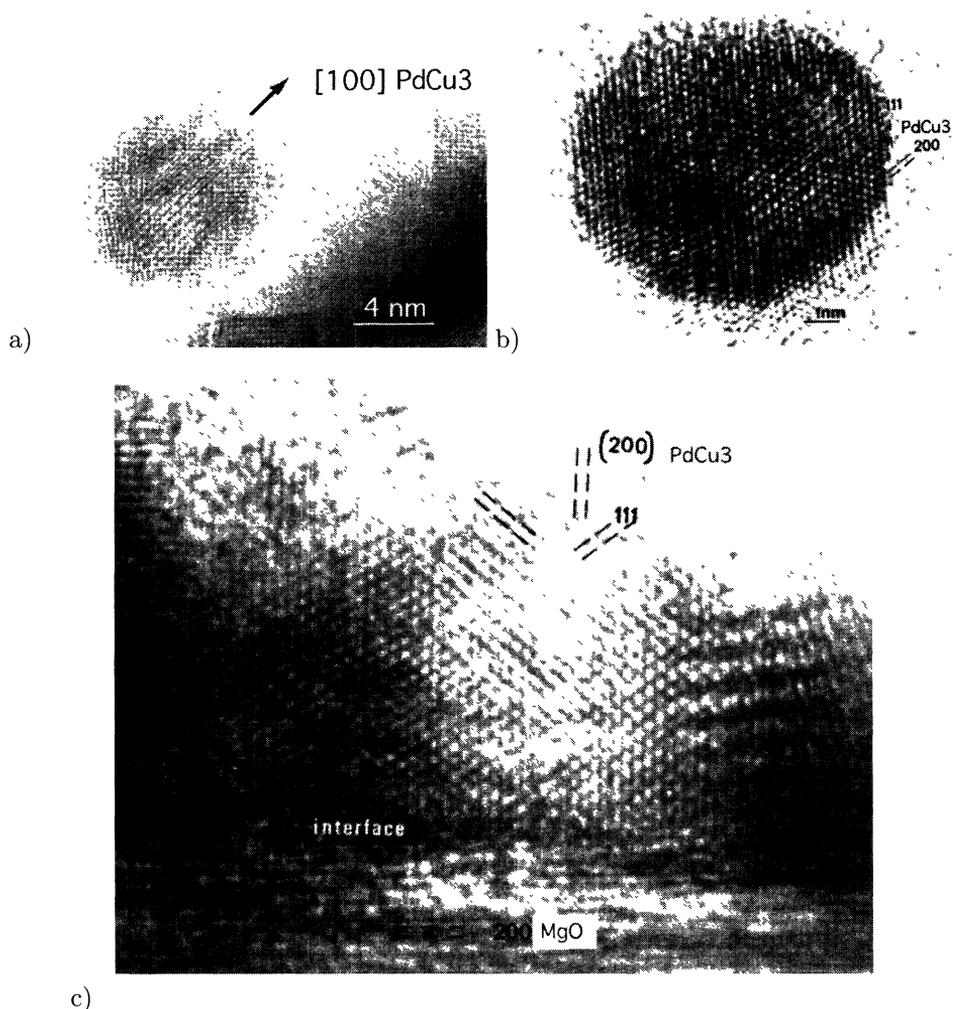


Fig. 9. — HRTEM images of PdCu<sub>3</sub> particles, (a) in top view, oriented (001) on MgO(001), (b) in top view, (110) oriented on MgO, (c) in profile view, oriented (110) on MgO(001), observed along a [110]PdCu<sub>3</sub> direction.

Another particle (11 nm), in the same (110) epitaxial orientation on MgO is seen in profile view (Fig. 9c), with (110)PdCu<sub>3</sub>  $\parallel$  (001)MgO and [100]PdCu<sub>3</sub>  $\parallel$  [100]MgO. The lattice does not show any phase boundaries.

## 5. Discussion

Bimetallic particles of Pd<sub>50</sub>Cu<sub>50</sub> and PdCu<sub>3</sub> were produced by wet impregnation of clean MgO micro-cubes.

The formation of PdCu particles (< 6 nm) was observed during annealing at different temperatures (from 350 to 500 °C), in reducing conditions. The particles grow first with the fcc structure, without definite shape until 400 °C. According to the phase diagram, the stable

structure at 350 °C for the alloy Pd<sub>50</sub>Cu<sub>50</sub> is the  $\beta$  ordered structure. The transition between the fcc solid solution and the  $\beta$  ordered structure only occurs after annealing between 400 and 450 °C. The observation of the disordered phase below 400 °C is certainly due to a kinetic effect. Even with other preparation techniques, the fcc structure was found at low temperature [13,16], on the other hand, above 400 °C, particles were found with the ordered  $\beta$  structure [3,16].

The particles, with the fcc structure and undefined shape, were found in two main epitaxial orientations on MgO(001), with (001)PdCu || (001)MgO, [100]PdCu || [100]MgO and (110)PdCu || (001)MgO, [100]PdCu || [100]MgO.

After annealing at 450 °C, all the PdCu particles have the  $\beta$  structure and are (001) oriented on MgO(001) with [110]PdCu || MgO[100]. The particles attain their final size by coalescence and present truncations at the edges by (100) and (110) faces.

The HRTEM images of the particles with the ordered structure on MgO, in top view and in cross-section and the image simulations, show that the atoms of metal are always aligned with the atomic columns of the MgO. In the  $\beta$  structure of PdCu, the (001) faces are only made of one type of atoms, Pd or Cu. From the HRTEM observations it was not possible to distinguish between these two cases.

The Pd particles (fcc) prepared by decomposition of organometallic compounds on MgO [14] were always found with a 4% dilatation of the lattice in the volume due to the reduction in H<sub>2</sub> and 8% at the interface corresponding to a perfect accommodation to the substrate. Here, the small PdCu particles (2-3 nm) with the fcc structure, (001) oriented on MgO after annealing at 350 °C, have the same lattice parameter as MgO (0.42 nm instead of 0.376 nm which is the parameter of the solid solution). So they are dilated by 10% and perfectly accommodated to the substrate.

After annealing at 450 °C, the PdCu particles size is larger due to the dynamic coalescence during annealing at higher temperature. In the bulk material, the misfit between the (110) lattice fringes of PdCu and the (200) lattice fringes of MgO is only +0.4% for the metal. Here, no dilatation is found neither at the interface nor in the volume of the particles. On the other hand, a slight contraction is measured, which is not specific to the alloy and certainly due to the substrate.

In the case of PdCu<sub>3</sub> particles with the  $\alpha$  ordered structure, even after 5 days of annealing at 500 °C, no regular shapes are obtained. Most of the particles smaller than 10 nm are epitaxially oriented (100) or (110) on MgO, without anti-phase boundaries in the lattice.

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