

## HREM-STUDIES OF THE MICROSTRUCTURE OF NANOCRYSTALLINE PALLADIUM

W. Wunderlich <sup>1)</sup>, Y. Ishida, R. Maurer <sup>2)</sup>

Institute of Industrial Science, University of Tokyo, Japan,  
1) Max-Planck-Institut für Eisenforschung, Düsseldorf, FRG,  
2) Max-Planck-Institut für Metallforschung, Stuttgart, FRG.

(Received July 24, 1989)  
(Revised December 12, 1989)

### 1. Introduction

Recently Gleiter and coworkers [1-3] showed that nanocrystalline materials with their crystal size of the order of a few nanometers possess rather unusual properties: Thermal expansion, elastic constants, fracture stress, ductility, diffusivity, etc. are differing distinctly from those of conventional polycrystalline metals. It has been suggested that the properties reflect an unusual nature of the grain boundaries in nanocrystalline materials. The structure, however, was found changeable. A mere annealing of nanocrystalline palladium at above 370 K resulted in a change in the Young's Modulus [4], which indicates structural relaxations.

The crystal structure of nanocrystalline materials has been studied conventionally by X-ray [5,6] and neutron [7] diffraction. The results are interpreted by assumption of a certain model structure of the grain boundary region. EXAFS- [8], Mössbauer- [9] and Positron-spectroscopy [10,11], on the other hand, gave information about the atomic structure. High resolution electron microscopy (HREM) studies (like [12,13]) can fill the gap in between: On one hand this method is sensitive enough to observe the atomic arrangements, on the other hand areas representative for the whole specimen can be chosen.

In this paper the microstructure of nanocrystalline palladium was examined by high resolution electron microscopy. A brief description of the specimen preparation and imaging of the lattice planes is given first. The special microstructure of the nanocrystalline palladium is characterized. The interest is focussed on the small crystals as well as on the grain boundary regions. The results will finally be compared with recent informations from other experimental techniques.

### 2. Experimental

The nanocrystalline palladium was produced by evaporation of Palladium in an inert He-gas atmosphere [14]. Small crystallites with a size of about 5-10 nm are obtained by condensation on the He-atoms. The crystallites are collected on the outer wall of a Cu-cylinder kept at liquid nitrogen temperature and compacted under high mechanical pressure (2.5 GPa) to disc like specimens at a vacuum chamber at  $P=0.1$  Pa [14]. The final density of the specimen is more than 85% of the bulk value. Small discs with a diameter of 2.8 mm and a thickness of 100  $\mu\text{m}$  were cut. The final thinning to get transparent TEM-foils was jet polishing with a 10 parts  $\text{H}_2\text{SO}_4$ , 9 parts HF aqueous electrolyte kept at 0°C and 30V applied. Even with this most preservable thinning method stress relaxation was suspected, however, mostly in the direction normal to the foil. HREM is not sensitive to this kind of structural changes. In the foil plane the twodimensional stress condition should be still maintained. Ion milling was not used to avoid irradiation effects.

The TEM-observations require a foil thickness smaller than the average grain size not just for optimal lattice imaging but mainly to prevent overlapping of grains in the image. This kind of "bamboo"-structure is encountered very close to the hole of the TEM-foil. The thickness of the TEM-foil at the observed area was estimated to be of the order of 3 nm by the movement of

characteristic points on the surface during tilting of the specimen. Hence, the thickness of the TEM-foil is less than that of the average grain size (radius 8.5 nm).

Imaging of the lattice planes is essential to distinguish individual grains. Palladium has fcc-structure with a suitable lattice constant of 0.388 nm. The spacing of the [111] planes ( $d = 0.224$  nm) as well as the spacing of the [220] planes ( $d = 0.194$  nm) lie above the resolution limit of the 200 kV high resolution electron microscope ( $C_s = 1.0$  mm) and can be imaged. A few micrographs were taken with a 400 kV microscope, in which the lattice planes can be imaged more stable at the Scherzër focus conditions.

### 3. Results

**(1) Fringe Visibility:** Fig. 1 is a typical high resolution electron micrograph of nanocrystalline Pd. Foil tilting experiments showed that the lattice image is visible for considerably large misorientations off axial or Bragg conditions in the case of the 400kV microscope and demonstrate its great capability. The fringes from the [111] planes, for example, remained for angles up to  $+8^\circ$  or  $-8^\circ$  by tilting perpendicular to the plane direction, depending on foil thickness. The maximum tilting angle for imaging the [200] planes is  $+6^\circ/-6^\circ$  and for the [220] planes less than  $+2^\circ/-2^\circ$ , respectively. These results agree qualitatively to previous observations on small Au-particles [15]. Two or three sets of lattice fringes appear in certain grains and allows to study the structure of grain boundaries. Moire pattern due to overlapping of lattice fringes were excluded from further studies.

**(2) Grain size:** Only limited regions in fig. 1 was without lattice fringes. By tilting the specimen about  $+3^\circ/-3^\circ$  in two directions it can be checked whether or not these regions consist of more than one grain. This procedure is essential to measure the grain size. Using a semiautomatic image analyser with a digitizer more than 100 grains were counted. The histogram can be fitted with a gaussian distribution on a logarithmic scale as it is expected from grain size measurements on conventional polycrystalline material. The average grain radius is 8.9 nm in one specimen and about 4 nm in another one, respectively. The values agree with those of the powder before sintering.

**(3) Voids:** The HREM-micrographs show, however, that not the whole volume is filled with grains. In fig. 1 several contrast effects with a round shape and a sharp border can be recognized either at grain boundaries or seldom smaller ones inside the grains. The size is about 0.1 - 1 nm, that is about 1/10 of the grain size. The area inside those circles appears brighter than the crystallites. Sometimes even a hole can be seen. Under HREM-conditions a brighter contrast is mainly caused by microvoids (better to say nanovoids), e.g. metal atom free volume. They may be formed during sintering. Diffusion of atoms in the bulk material as well as along the surface of the voids would be able to form the round shape during the time of about 10000 h before the HREM-observation of the nanocrystalline palladium. It can not be excluded that smaller pores may be enlarged in size during the preparation process of the thin TEM-foil, if they lie on the surface of the specimen. The triple line, where three grains meet together, usually are filled with atoms in a crystalline order. Voids are sometimes observed and rather seldom an amorphous region appears. This is an evidence that weak bonded regions like amorphous areas are not destroyed by the thinning process.

**(4) Grain boundary structure:** The atomic structure of grain boundaries can be determined only, when the electron beam incidences parallel to the grain boundary plane and the boundary plane itself is parallel to low index zone axes of at the neighbouring grains. These conditions are satisfied only seldomly in special grain boundaries. Grain Boundaries in nanocrystalline materials, however, occasionally fulfill such conditions and periodical structures are sometimes noticed. Even the smallness of the grain radius cannot suppress the occurrence. Structural periodicity is important for a detailed analysis of grain boundary structures by comparison with calculated HREM-images of assumed structures [13]. The micrographs (fig. 2) show in most cases a qualitative difference in the contrast in a vicinity of more than 0.6 nm at general grain boundaries compared to conventional polycrystalline material. Explanations for this loss on brightness and sharpness might be an extended grain boundary region similar like amorphous regions or any shifting of the atoms near the boundary away from the crystalline positions due to internal forces. However, curvature in the direction of the incident beam or similar atomic arrangements might be possible as well. The expression "wavy" grain boundary might characterize best a curvature with a radius smaller than the grain size. Grain boundaries in nanocrystalline materials certainly are at high energy states. These types of grain boundary structures are not observed in conventional polycrystalline material.

**(5) Local stresses:** In most cases the lattice planes near the grain boundary are slightly distorted which indicates local stresses in the grain boundary region. Other grains contain several areas where the brightness of the lattice planes differ very much. The fringe contrast (not the visibility mentioned above) in HREM depends very sensitive to local changes of orientation indicating bending of the grains due to high internal stresses. Evidence for relaxed internal stresses shows fig. 2a: In these regions, shear stress is mainly reduced by twin formation in three neighboring grains. The double hatched areas in the schematic drawing (fig. 2b) indicate bended regions, the arrows indicate the direction of internal stresses. The mechanical twinning may happen in the nanocrystalline material during the sintering process under high mechanical pressure.

**(6) Dislocations:** Sometimes isolated dislocations or dipoles (fig. 3) are detected inside the grains. The core of the dislocations is smeared out to about two elementary cells,  $\sim 0.8$  nm, as far as the contrast of HREM-images can be naively interpreted. Obviously the observed edge dislocations are immobile, because stresses from surrounding grains are too strong. Even small angle grain boundaries (often not in straight lines) consist of several edge dislocations. The mean dislocation density is more than  $10^{15}$   $1/m^2$  which is hardly reached in plastically deformed metals.

The lattice imaging technique shows some interesting aspects which can hardly be detected by other experimental techniques. As a rough estimate the microstructure of as received nanocrystalline palladium contains about 40 Vol-% undistorted crystalline areas, 25 % extended or amorphous like grain boundary regions, 25 % regions with high internal stresses and about 10 Vol-% pores.

**(7) Annealing behaviour:** Heating experiments were performed to check the stability of the nanocrystalline palladium. Firstly a bulk specimen was heated to  $1300^\circ\text{C}$  in a quartz tube and prepared for HREM observations. Nearly 99 % of the previously nanocrystalline palladium has recrystallized in grains of about  $0.5\text{--}1\mu\text{m}$ . The transition between the recrystallized part and the remaining nanocrystalline grains was sharp. No intermediate "buffer" grains are observed. The recrystallization front is rather wavy and follows the nanocrystalline grains.

In a second experiment a thin TEM-foil was annealed at  $800^\circ\text{C}$  for 1 h in high vacuum. This experiment may not be representative for bulk specimens, because by surface effects [16] smaller grains than in a bulk specimens remained in the thin foil. Nevertheless the obtained micrographs show the disappearance of bended regions within grains. Small angle grain boundaries and dislocations vanished, but twin boundaries were still present. Pores were also observed either at grain boundaries, triple lines or even within some grains. The recrystallization front did not annihilate the pores. The structure of grain boundaries has changed. The boundary plane became straight and absent in distorted regions as in conventional polycrystalline metals. The stable configuration of the grain boundary structure seemed to be reached.

#### 4. Discussion

The above results showed that the structure of nanocrystalline palladium differs from that of conventional polycrystalline palladium and from the conventional description established by spectroscopic studies [5-11]. The discrepancy may be indicated only by two possibilities: either (1) these spectroscopic results may be reexamined in the light of the high amount of distortions, dislocations and voids observed in the present experiments, or (2) the present observations may be not fully reliable by concluding structural changes during preparations of the thin foil specimen. Both possibilities will be discussed.

Most surprising was the high amount of stressed regions and the high dislocation density. Within bulk nanocrystalline specimens the internal stresses might even be higher, because during preparation of TEM-specimens stresses can relax and dislocations are shorted by image forces and surface effects. The electrochemical thinning process has been considered as most likely mechanism. A considerable amount of experiences, however, have been accumulated on the possible structural change of thin foil specimen during HREM study of amorphous metals [17]. Micrographs of ion milled specimen, for example, were found controvertible [18], because the atomic structure of surface layers is affected. Electrolytically thinning on the other hand was considered free from such problems. Observation of distorted layers in the present specimen should be an indirect proof that the structure did not relax during the thinning and indicate the presence of internal stresses.

During observation with the high density electron beam palladium specimens are stable except if they are heated. However, silver nanocrystals, for example, were found to grow during TEM-observation [15].

By positron spectroscopy of several nanocrystalline metals [10,11] a positron life time  $\tau_1$  was measured which corresponds to a free volume of the size of about a lattice vacancy. The core of a dislocation line has about this size. The rather high amount of observed dislocations agree to the results from positron spectroscopy. Moreover voids of the size of ten vacancies and others in the size of grains were detected by positron spectroscopy. Both kinds of pores can also be observed in the HREM-micrographs. The amount of about 10 Vol% may explain part of the density deficit of the nanocrystalline material below that of conventional Pd besides the effect of the lower density in the interfacial regions. Another evidence for the presence of these pores is the chemical measured oxygen-content in nanocrystalline palladium of typical 1-2 at% [19]. With Auger Spectroscopy (AES), however, no oxygen segregation was recorded along fracture surfaces along grain boundaries [19]. The low affinity of  $O_2$  to Pd may lead to  $O_2$ -precipitates which causes or at least stabilizes the pores in the material. However, it is controversial, why the X-ray experiments [5,6] do not show evidence for the pores. The broadened intensity peaks for small scattering angles as well as for high angles could be fit quite good by assuming an extended grain boundary region. The elastically or plastically distorted regions should also contribute to the broadening in the peaks.

The structure of grain boundaries within nanocrystalline palladium appeared in the HREM-micrographs different from conventional polycrystalline palladium. Most grain boundaries seem to have the extended grain boundary region as obtained by previous investigations [12,13]. X-ray-scattering on nanocrystalline Iron [5,6] showed an increased background intensity besides the discrete maxima in the intensity due to the scattering from the crystallites. The authors found the best fit to these data by assuming that the two outer layers of each crystallite was displaced in random directions. The authors pointed out, that the experimental data could not be fitted by assuming short range order within the interfacial structure. These results are consistent to small angle neutron scattering- [7], Mössbauer- [9] and EXAFS-experiments [8] on nanocrystalline Cu and Pd, where a lower density in the grain boundary region was detected. Mütschele and Kirchheim [20] measured the amount of Hydrogen segregation and found values between 0.8 to 1.1 nm for the thickness of the grain boundary region. HREM-micrographs of grain boundaries show in general a smaller thickness of 0.6nm or 0.4nm as found by Thomas et al.[13]. Caution is announced, since in many cases wavy or curved boundaries prevents an exact atomic structure analysis. Results obtained by indirect methods, however, should be checked whether the presence of stressed regions and voids as observed in the present experiments would allow a fit to thinner grain boundaries. In the nanometer sized crystals the ordering of the grain boundary structure by minimizing the interfacial energy is suppressed, since the curvature of the grain boundary has a much bigger effect on the energy. EMK measurements [19] proved that the free energy in nanocrystalline palladium is increased compared to conventional or monocrystalline Pd due to the particular grain boundary structure of the nanocrystalline material. The atoms inside the grain boundaries possess entropies comparable to those of gases. Annealing of the nanocrystalline specimens lead to an energy (and entropy) diminution indicating the metastable state.

More detailed studies with HREM or other techniques may focus in future more about the internal stresses in the grain boundary regions. Other interesting questions may be solved by HREM whether there is any texture or any ordering influence between the low index lattice planes of two neighboring crystals.

### 5. Conclusions

- 1) HREM of nanocrystalline palladium in the as received and electrolytically thinned state indicates presence of rather high internal stresses as can be seen by the high density of twins, small angle boundaries, dislocations and bent regions especially close to the grain boundaries.
- 2) The structure changed upon annealing: Normal coarse grain specimens with thin boundaries and undistorted grains resulted.
- 3) The low density of nanocrystalline palladium can be partly explained by pores, partly by an extended grain boundary structure.

### 6. Acknowledgement

The authors would like to thank Prof. H. Gleiter, Universität Saarbrücken, and Dr. H. Ichinose, University of Tokyo, for usefull discussions and Mrs. U. Bäder for experimental assistance. The JEOL Company is gratefully acknowledged for using the 400 kV HREM-microscope. The work was supported by a fellowship of the Institute of Industrial Science, University of Tokyo, which is gratefully acknowledged.

### 7. Literature

- [1] Rainer Birringer, Ulrich Herr, Herbert Gleiter, Nanocrystalline Materials - a first report, Proceedings of JIMIS 4 (1986), Suppl. of Transact. of Jpn. Inst. of Metals, **27**, (1986), pp. 43
- [2] Rainer Birringer, Herbert Gleiter, Nanocrystalline Materials, in: Encyclopedia of Material Science and Engineering, Suppl. Vol. 1 ed by R.W. Chan, Pergamon Press 1988, pp. 339-349
- [3] H.-E. Schaefer, R. Würschum, R. Birringer, H. Gleiter, Structure and properties of nanometer-sized solids, to be published Physical Research, Akademie-Verlag, Berlin, G.D.R.
- [4] M. Weller, H.-E. Schaefer, Proc. Deutsche Physikalische Ges., Karlsruhe, 1988, M-26.2
- [5] X. Zhu, Ph. D. Thesis, (1986), University of Saarbrücken
- [6] X. Zhu, R. Birringer, U. Herr, H. Gleiter, Phys. Rev. B **35**, (1987), pp. 9085-9090
- [7] E. Jorra, H.Franz, J.Peisl, G.Wallner, W.Petry, T. Haubold, R. Birringer, H. Gleiter, Phil. Mag. B, **60**, (1989), pp. 159-168
- [8] T. Haubold, B. Lengeler, R. Birringer, H. Gleiter, Phys. Let. A, **135**, (1989), pp. 9545-ff
- [9] U. Herr, J. Jing, R. Birringer, U. Gonser, H. Gleiter, Appl. Phys. Lett., **50**, (1987), pp. 472
- [10] H. E. Schaefer, R. Würschum, Physics Letters A, (1987), **119**, No. 7, pp. 370-374
- [11] R. Würschum, M.Scheytt, H. E. Schaefer, phys. stat. sol. (a), **102**, (1987), pp. 119-ff
- [12] R.W. Siegel, S.Ramasamy, H.Hahn, L.Zongquan, L.Ting, R.Gronsky, J.Mat.Res. **3** (1988) pp.1367
- [13] G.J. Thomas, R.W. Siegel, J.A. Eastman, Proc. MRS-Meeting, Spring 1989
- [14] C. G. Granquist, R.A. Buhrman, J. Appl. Phys. **47**, (1976), pp. 2200-ff.
- [15] Y. Ishida, to be published
- [16] H. Fujita, M. Komatsu, In-situ-Observ. of recryst., Proc. Int. Conf. Sintering '87, Tokyo
- [17] Yoishi Ishida, Hideki Ichinose, J. Electron. Microsc., **34**, (1985), pp. 266-276
- [18] M.J. Kim, R.W. Carpenter, Ultramicroscopy, **21**, (1987), pp. 327-334
- [19] R. Kirchheim, private communication
- [20] T. Mütschele, R. Kirchheim, Scripta. Met., **21**, (1987), pp. 1101-1104

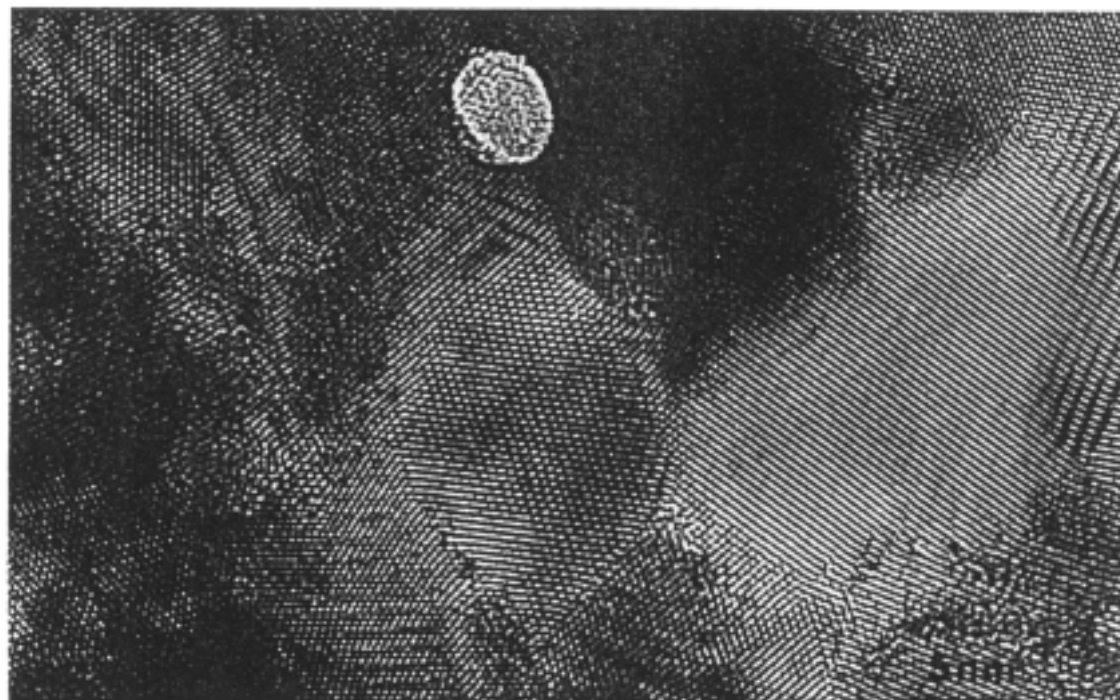


FIG. 1) High resolution electron micrograph of a typical region in nanocrystalline palladium imaged at 400 kV. On the right side a small angle grain boundary can be identified. The round bright circles are pores probably grown during the sintering.

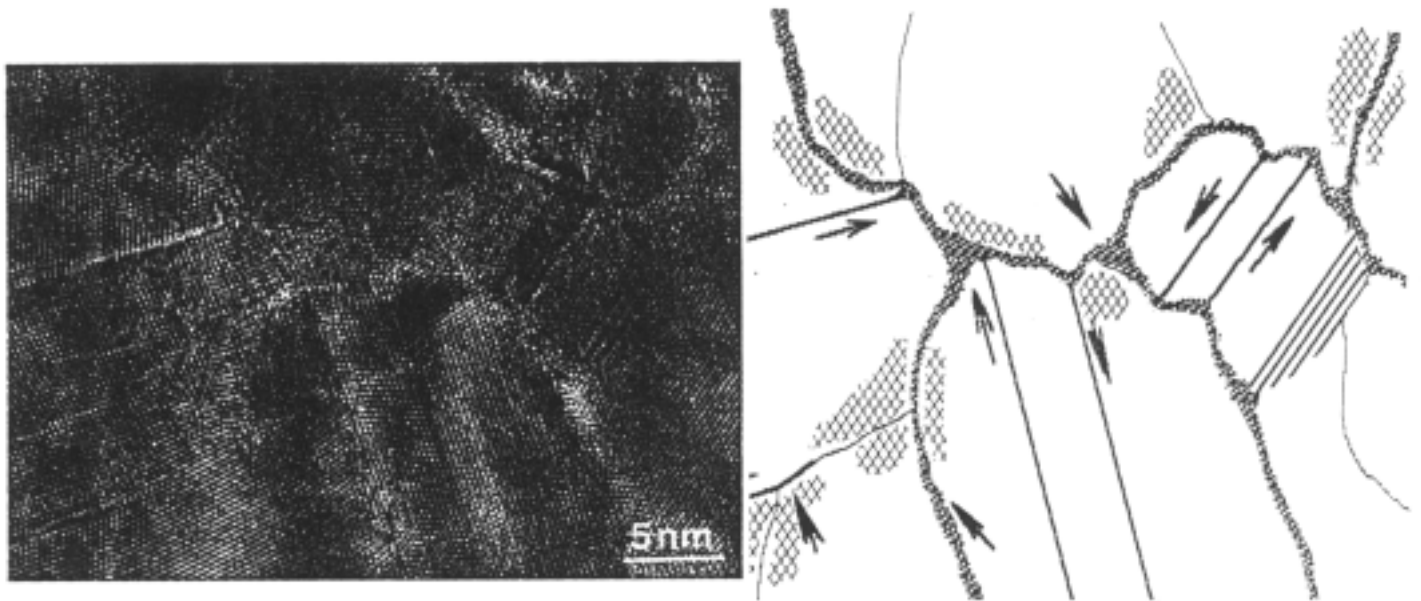


FIG. 2) In three of these grains twins are nucleated probably by shear stresses during sintering the nanocrystalline powder. The thickness of general grain boundaries has a size of more than 0.6nm. The double hatched areas in the schematic drawing indicate bended regions, the arrows indicate the direction of internal stresses.

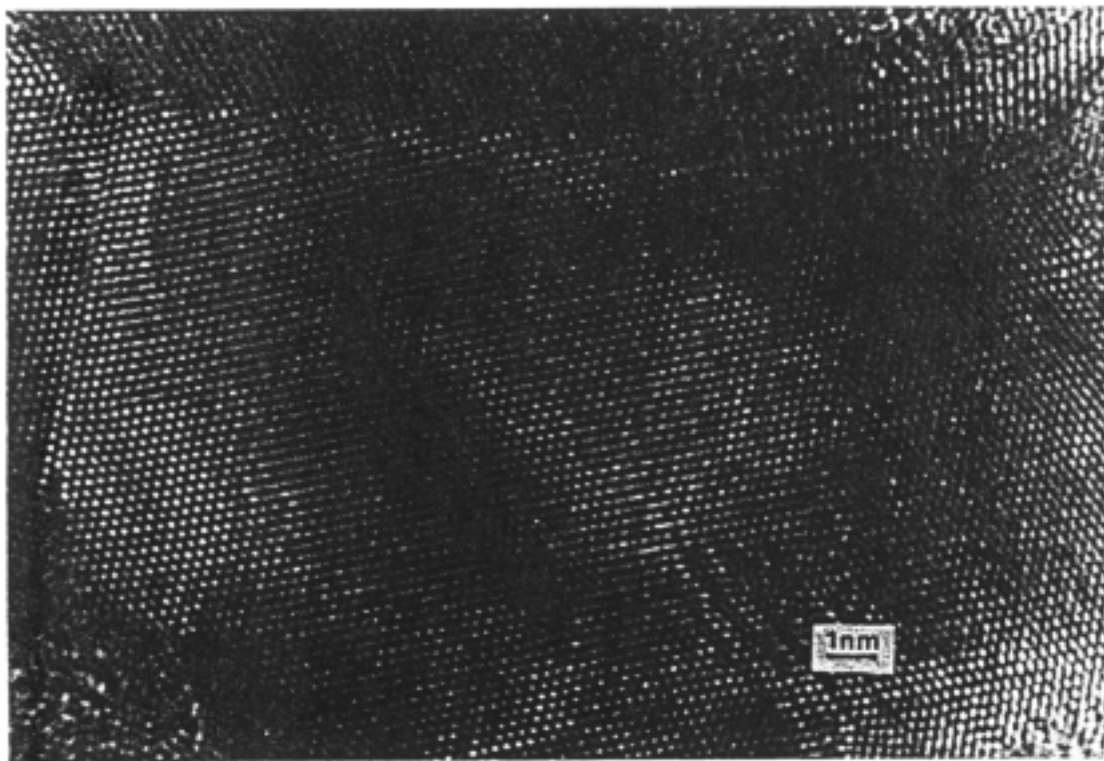


FIG. 3) In several cases dislocation dipoles were found inside a grain.