Rietveld analysis of policrystalline materials using precession of electron diffraction

G. PRODAN, V. CIUPINA
"Ovidius" University of Constanta, Mamaia Avenue No.124, 900527, Romania
gprodan@univ-ovidius.ro

Abstract

Powder diffraction is one of the methods most used for structural analysis of polycrystalline materials (thin films or powders). The Rietveld method was developed for neutron diffraction analysis and adopted later for X-ray diffraction. Recently, the method was accepted and used in electron diffraction analysis. Electron diffraction powder patterns are difficult to analyze and experimental data must be carefully select. The dynamical effect is one of the perturbing factors in Rietveld analysis of electron diffraction data, resulting from scattering of electron in large crystals or crystalline defects. Electron diffraction studies have the advantage that can be used in the same time with morphological study of the working area, or it can be related with high resolution mode. Precession of electron diffraction was developed recently and acquired diffraction pattern are close to kinematical theory, as required in Rietveld analysis.

Electron microscopy use copper / nickel grid coated with a layer of amorphous carbon or formvar as support for samples. Nanopowders are prepared from dilution in alcohol, after ultrasonication, by depositing a drop of dilution on formvar or carbon. The same method can be applied to nanostructured films. If the sample geometry requires examining nanostructures-support geometry, they must be thinned so the final thicknesses will be 10 nm. Thinning is done by cutting (ultramicrotomy), electrochemical etching or ion milling.

We use Rietveld refinement method on data obtained by electron diffraction from gold nanoparticles supported by amorphous carbon and thin aluminum film on formvar support. Both materials were obtained by vacuum evaporation. The average dimensions obtained from TEM images are 10 nm for gold nanoparticles and 39 nm for aluminum film. Also, we make a comparative study on data obtained in classical electron diffraction and those obtained using precession of electron diffraction (PED). We observe immediate improvement in case of PED intensities, which are close to the calculated value of the geometric approximation. It also introduced a new way of obtaining DARK FIELD imaging using precession electron diffraction.

Keywords: powder, Rietveld, precession, electron diffraction, dark field

Introduction

The determination of crystal structure at the atomic scale is a fundamental step to understand the properties of materials. Precise knowledge of diffraction line-profile is of utmost importance in powder diffraction especially in line-broadening analysis and Rietveld refinement. The fact that electrons, unlike X-Ray can be focused into an image was exploited in the invention of electron microscope (KNOLL & RUSKA, [1],RUSKA, [2]. The ability to form images in the electron microscope makes it very powerful for looking at non-crystalline as well as crystalline materials. Today is known that electron microscope could reveal detailed aspects of living cell, with a resolution 100 times higher than the light microscope (PORTER & al, [3]. For crystals, the situation was different, until the resolution of electron microscope was lower than 4Å in 1970. Today, study of inorganic crystals can be performing in new generation of electron microscope at 0.7 Å resolution or lower.

Electron diffraction has advantages that crystals size can be very small and the phases of crystallographic structure factors, which are lost in X-Ray diffraction, are present in transmission electron microscopy. In powder electron diffraction we can use the same concepts developed for X-ray diffraction or neutron. Basically, Bragg's law is verified by electron diffraction. Differences are observed at diffracted beam intensities, which are different from those obtained from X-ray diffraction, due to fact that the electron scattering occurs on the whole atom, while X-ray diffraction is result of interaction between photons and atom electrons. Scattering factor varies and thus has different diffracted intensities distribution. However, if we mean only the quantitative value of the intensities these phenomena produce a similar result.

Rietveld method was imposed in crystallography, initially as a method for studying materials using neutron diffraction (RIETVELD, [4]. It was quickly adopted for X-ray diffraction. She emerged as one of the methods which ensure proper processing of experimental data and due to the evolution of computer and software solutions, the method was implemented to study materials properties, crystalline structure refinement, line-broadening analysis, absorption and microabsorption, magnetic scattering calculation. Fullprof (CARVAJAL , [5] and Fox [FAVRE-NICOLIN,& CERNY, [6] are only two examples. Also, we can remember GSAS[LARSON, & VON DREELE, [7], DBWS[BLEICHER et al. [8], Jana2000[PETRICEK et al. [9] application that implement Rietveld refinement and other structural investigation.

Materials and methods

We use fine copper grid covered with a layer of formvar or amorphous carbon as a support for our samples. Sometimes, nanostructured films require prior preparation. An example is thin film obtaining by evaporation on large substrate, e.g. Si support with 508 mm thickness or glass commonly used in the deposition of thin films. The quickest and easiest method is by scratching the film with a diamond knife in the area put a drop of alcohol or water and then place the grid coated substrates [TEODORESCU, & BLANCHIN, [10]. Micro or nano-sized pieces from scratched materials are glued to the support due to surface forces. The method is practical when seeking structural analysis of film, as required in powder diffraction. The disadvantage is the contamination of sample with pieces from support.

Gold nanoparticles were directly deposited by vacuum evaporation onto amorphous carbon. Aluminum films were deposited by evaporation directly on formvar coated grid and on the ceramic substrate. For the film deposited on ceramics we used the method described above to obtain grid for electron microscopy investigation. Samples were investigated by Philips CM120ST microscope at a voltage of 100kV, in conventional transmission electron diffraction and electron diffraction with and without the precession (P020 SpinningStar Nanomegas system). We used specialized applications ITEM, CRISP2, Fox and package Fullprof for processing experimental data and Rietveld analysis.

Results and discussions

Dimensions of gold nanoparticles are distributed around 10 nm value determined by measuring the diameters of BFTEM (Bright Field Transmission Electron Microscopy) images (Figure 1). Aluminum films have distribution of grains around 39 nm for film deposited on formvar and 145 nm for film deposited on the ceramic (Figure 2).

To observe the effect of substrate on the intensity of diffracted beams we made an experiment using gold nanoparticles deposited on amorphous carbon film. In the first phase

we acquired an electron diffraction with beam-nanoparticle-substrate geometry (noted as UP geometry), followed by a substrate-nanoparticle-beam geometry (noted as DOWN geometry). These geometries are illustrated in Figure 3 related to incident beam (green arrow).
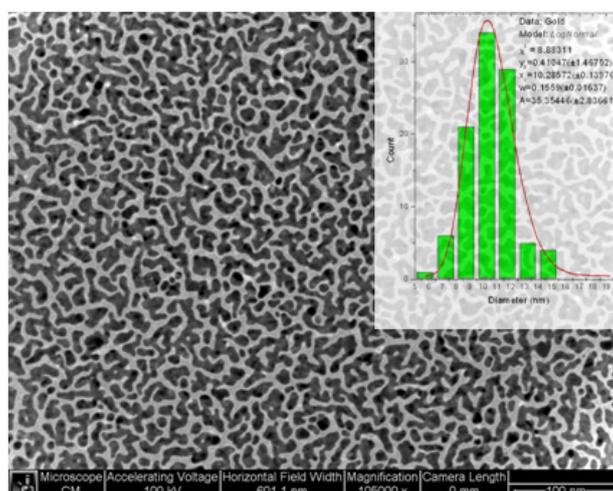
Figure 1. *Distribution of gold nanoparticles on the carbon film and histogram of measured diameters with lognormal fit curve (red)*
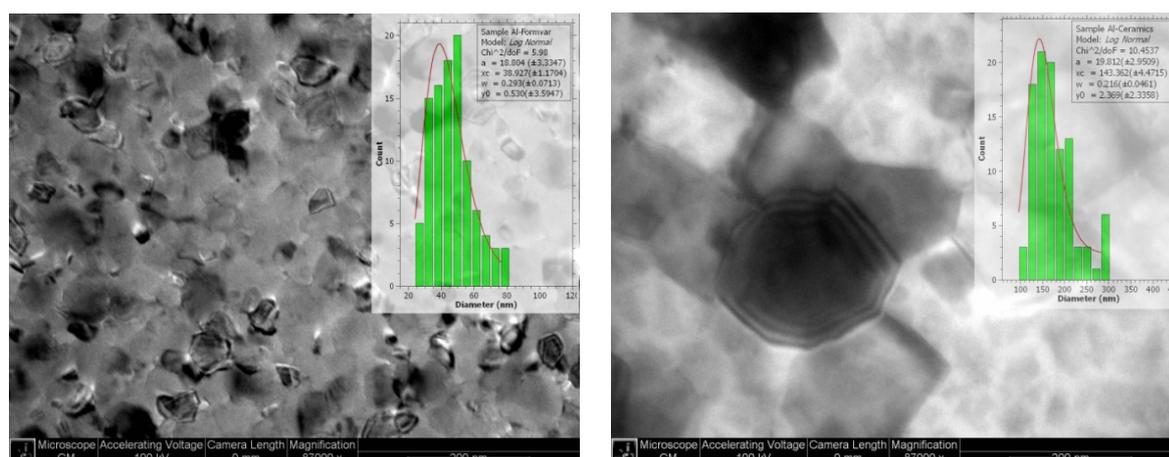

Figure 2. *a) Aluminum film deposited on formvar grid. b) Aluminum deposited on ceramic with histograms inserted*

The TEM images of the sample are inserted in figure to show a damaged area on the film selected as point of reference. In the right side are diffraction pattern and profiles extracted using CRISP2 application. In Table I we present values of intensities and interplanar distances experimental determined compared with calculated values.

Table 1.

| d_{hkl}(UP)	I_{hkl}(UP)	d_{hkl}(DOWN)	I_{hkl}(DOWN)	d_{hkl}	I_{hkl}
2.3604	8191 (100)	2.3161	11884 (100)	2.3546	100
2.0538	2931 (35.78)	2.0140	4593 (38.64)	2.0391	49
1.4412	2356 (28.76)	1.4143	3532 (29.72)	1.4419	33
1.2312	2230 (27.23)	1.2079	3340 (28.11)	1.2296	39
1.1786	514 (6.27)	1.1568	747 (6.29)	1.1773	11
1.014	88 (1.074)	0.9974	141 (1.18)	1.0196	6

We can see that higher intensities of diffracted beams for DOWN geometry because in the UP geometry case, diffracted beams are affected by diffuse scattering on amorphous substrate. In DOWN geometry, diffuse scattering affect only the incident beam. Resulted beam is distorted again by material, and follow the Bragg conditions. We will have such behavior when sample are build by a completely random distribution of crystals.
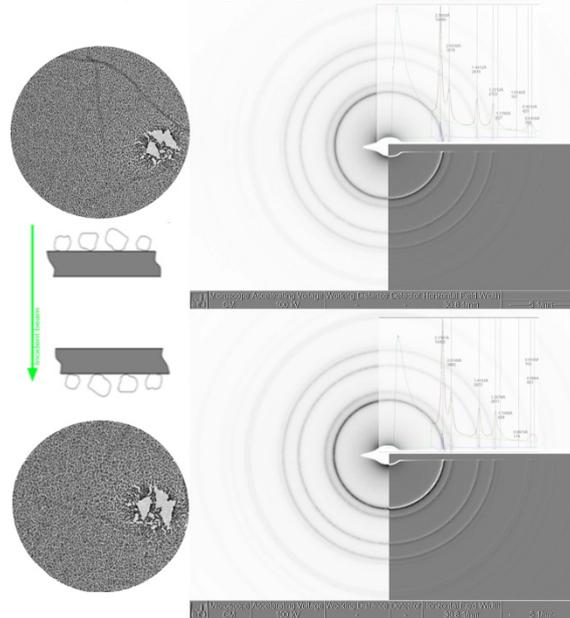
Figure 3. *Experiment to reveal sample-support geometry effects on the intensity of diffracted beams*

Also we note a difference between determined interplanar distances. This can be explained by the fact that we kept the sample in same eucentric point, so in both cases we use the same calibration constant. This will change the parameters involved in calculation of interplanar distance, like camera length.

In figure 5 ratio of experimental intensities are represented graphically compared with values calculated using a zero order Bessel function to highlight the dynamic effects in the sample. The ratio of beam intensity in kinematical approach and intensity when dynamic effects occur is given by Blackman's (Figure 5 inset formula) (BLACKMAN [11]

$$\frac{Idyn}{Ikin} = \frac{1}{A_h} \int_0^{A_h} J_0(2x)dx$$
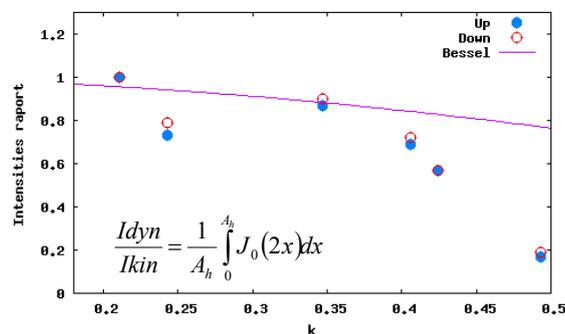
Figure 5. *Intensities ratio (to maximum intensity) in UP and DOWN geometries relative to Blackman curve (all value scaled to unit).*

A new method is used to acquire electron diffraction figure by mean of precession of electron diffraction. Method improves the obtained experimental data also for polycrystalline material. The following are experimental data obtained on crystalline gold nanoparticles

deposited on amorphous carbon film and we used DOWN geometry to compare acquired data without and with precession active (Figure 7).
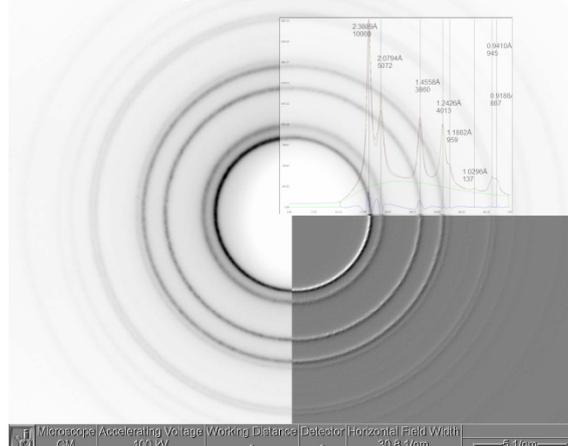

Figure 7. *DOWN geometry with precession*

Table II present experimental results in DOWN and PED-DOWN geometry versus calculated values.

Table 2.

d_{hkl}(DOWN)	I_{hkl}(DOWN)	d_{hkl}(PED)	I_{hkl}(PED)	d_{hkl}	I_{hkl}
2.3161	11884 (100)	2.3889	19158 (100)	2.3546	100
2.0140	4593 (38.64)	2.0794	9717 (50.72)	2.0391	49
1.4143	3532 (29.72)	1.4558	7396 (38.61)	1.4419	33
1.2079	3340 (28.11)	1.2426	7689 (40.13)	1.2296	39
1.1568	747 (6.29)	1.1882	1839 (9.60)	1.1773	11
0.9974	141 (1.18)	1.0296	262 (1.37)	1.0196	6

When precession is active we observed the fact that intensity ratio is above the Blackman reference curve (Figure 8). This is immediately seen from the table II, if precession values were greater than those calculated.
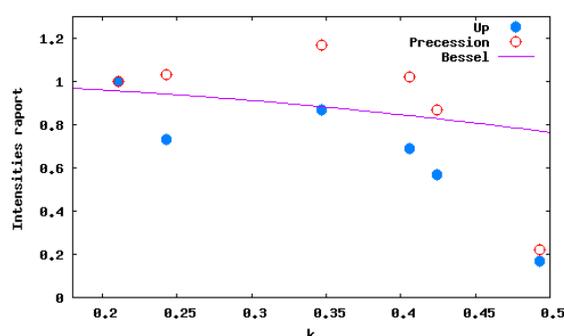

Figure 8. *Intensities ratio behavior in DOWN and PED cases*

At greater angles, intensity value decreases, being close to the classic case. This can be explained by means of Ewald sphere, which limit intensities visible to detector (CCD camera). We use Fox and FullProf applications to perform crystal structure refinement of materials starting from a known model. Among the important results achieved by these applications include electronic density calculated using Fourier series based on experimental data extracted from electron diffraction image (Figure 9). To check the correctness of the

electronic density distribution we built same map for a unit cell using SIESTA code (D. SANCHEZ-PORTAL, [12].

Distribution obtained using SIESTA code is observed to decrease to zero inside the atom. This is due to pseudo potential selection. We built pseudo potential on assumption that atom is composed by a virtual nucleus (real nucleus plus core electrons) and valence electrons, at 300K temperature.
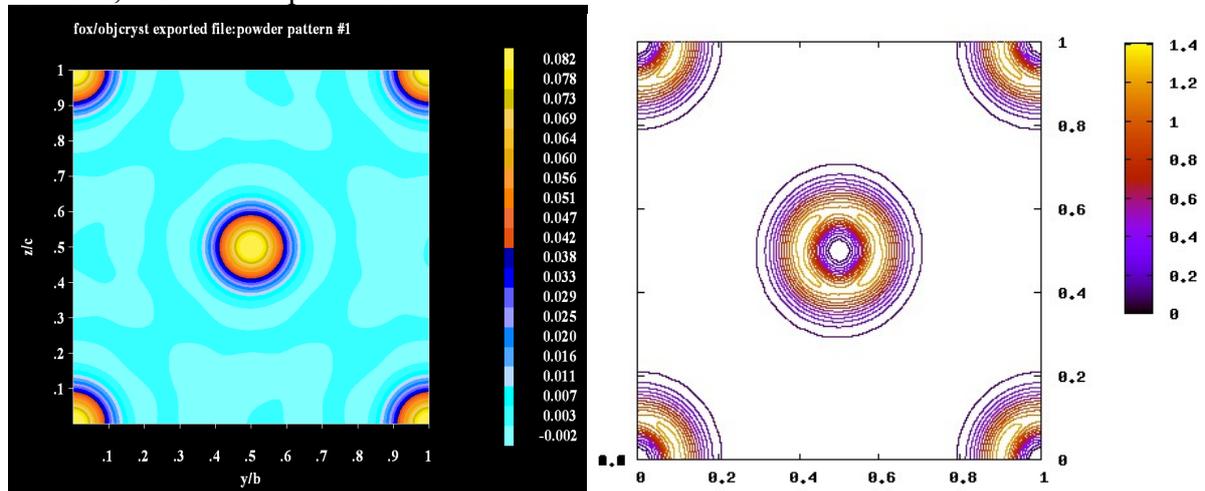
Figure 9. *Electronic density using GFourier FullProf package (section on one face of the cube and cube in the middle section) electron density calculated using discus package (up) and SIESTA code (down)*

DarkField (DF) module helps to identify crystalline areas on studied material. This is achieved by identifying high brightness areas in TEM image. DF image is formed by diffracted beams on predetermined directions. We use three ways to build DF images (Figure 10):
- OBJ - objective aperture is used to select diffracted beam
- DF - microscope implemented DF mode, with angle set for (111) planes
-DF + P - DF image acquires with precession active and diffracted beams restricted by combination of objective aperture dimensions and angle of precession
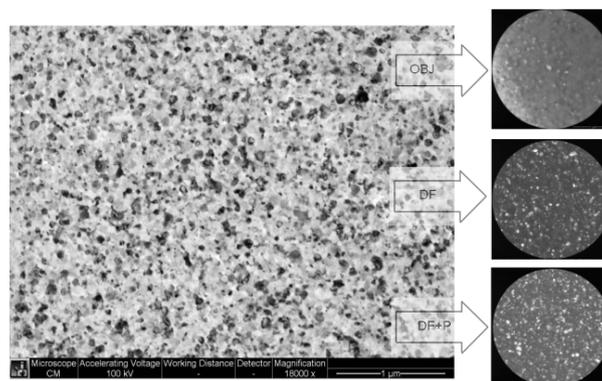
Figure 10. *Crystalline aluminum thin film and DF modes*

Conclusions

Electron microscope has the most varied applications. Electron diffraction on crystals is a complement to information about their structure, obtained by means of other techniques, like X-ray or neutron diffraction. There is also the contamination danger, if the electrons heat the material, but this can be relatively easily avoided by ensuring optimum working

conditions, like using liquid nitrogen to cool down sample area. Also we can use a low intensity beam, which is possible by means of apertures.

Crystalline structure is one of the important parameters in characterizing a material. Refining, improving the values that describe the crystal structure has been successful in studied cases, the negative effects of dynamical theory is very low. Thus, the Rietveld method can be successfully applied for electron diffraction, but only if the studied material can be described using kinematical approximation.

Lattice parameters was determined with relatively small errors ~0.5% in case of gold standard. Rietveld method using these cell parameters was successful used for future construction of Fourier maps and electronic density.

As a conclusion we can say that mathematical algorithms implemented in new generation of PC are useful tools in crystallographic tasks: determination of lattice parameters, refinement of structures, physical properties derived from crystalline structure. This work is the result of research projects MATSTOM 71-070/2007 and NANCARB 71-121/2007.

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