

Application of ordinary powder diffraction to examination of extraordinary properties of nanocrystalline materials (2h)

Bogdan PALOSZ

Institute of High Pressure Physics UNIPRESS, Polish Academy of Sciences

Labeling a group of materials as "nano" is justified if their properties are unique in the sense that they cannot be described or explained based on the rules (theories, formulas, etc.) which apply to "ordinary" materials. A distinction between "nano" and "non-nano" materials emerged and became common only in the last two decades, and that happened not because "nano-materials" did not exist before, but because the scientific community always demands new research directions which are worth to concentrate on and which require solving specific problems. Development of technologies of fabrication of nano-materials and of the methods of their characterization reached the point where examination of nano-sized objects became possible. This concerns in particular the resolution/accuracy level required for (i), technologies of the synthesis of objects with well controlled dimensions in the range of a few nanometers; (ii), direct observations of such nano-objects; and (iii), measurements of the materials properties associated with their small volume and/or physical dimensions. Nanoscience begins when properties of the material can no longer be described using conventional tools, in particular using relationships derived for ordinary materials. In other words, we deal with nanoscience when a given property is clearly related to the small characteristic dimension(s) of the object.

The basic and essentially only technique for determination of the atomic structure of matter is diffraction. A complex structure of nanomaterials causes, that standard methods of structural analysis are of limited use and non-standard and new approaches and tools for structural analysis are necessary. Relative to standard crystalline materials a nanocrystal is not a single crystal but it constitutes a unique object: (i), its structure is different in the bulk than at the surface, and (ii), the grain size limits long-range interactions to the characteristic dimension(s) of the individual grain only. For the above reasons, the structure of a nanocrystal cannot be approximated by a model of an ideal crystal lattice. In practice that means, that any structural analysis of such materials has to be based on "total scattering", which comprises both coherent and incoherent components. Certainly, it is not always necessary to examine total scattering since useful information about the structure of nanocrystals can be obtained from the analysis of characteristic Bragg scattering also. It should, however, be realized that such information is definitely incomplete since it refers only to coherently scattered part of the diffraction pattern which reflects the crystalline part of the sample volume.

There is a variety of specific problems that might address diffraction structural studies on nanocrystals: (i) what is the nanocrystal basic crystallographic structure, (ii) what are the differences between similar crystal phases present in nano- and micro- polycrystalline samples (if those differences really exist), (iii) what lattice defects are present in nanograins, and, finally, (iv) how to verify a presence of the core-shell structure which discerns between the grain interior and its surface, if such model is applicable.

It is quite natural that working in the field of experimental powder diffraction, we are well aware of the shortcomings imposed by diffraction methods both by their technical limitations and by the available methods of elaboration of the experimental data. Those limitations affect our ability to set novel tasks and envision new research horizons. Therefore it is worthwhile to go beyond those limitations and embrace a different point of view, where "impossible is possible". Such opportunity is brought about by numerical simulations, i.e. a virtual experiment without technical limitations of experimental reality. It is the area of a great potential which has essentially not been applied to studies on nanomaterials yet. It can be a tremendous inspiration for experimenters, crystallographers, and a great opportunity for the modelers to verify their theoretical predictions.

References

B.Palosz, S. Stelmakh, E. Grzanka, S. Gierlotka, W. Palosz, "Application of the Apparent Lattice Parameter to determination of the Core-Shell Structure of Nanocrystals", *"Nanocrystallography"*, in: *Z.Kristallography*. 222 (2007) 580-594.

B. Pałosz, E.Grzanka, S.Gierlotka, M.Wojdyr, W.Palosz, T.Proffen, R.Rich and S.Stelmakh, "Looking beyond limitations of diffraction methods of structural analysis of nanocrystalline materials" *Proc. of the IUTAM Symposium on Modelling Nanomaterials and Nanosystems, Springer Science+Business Media .V., Ed.R.Pyrz and J.C.Rauhe, pp.75-88*

Nanocrystals under high-pressure; in situ diffraction studies (1h)

Bogdan Palosz

Institute of High Pressure Physics, Polish Academy of Sciences

High pressure is a unique tool which might serve for investigation of interatomic interactions: high pressure suppresses the interatomic distances and, thus, "forces the material" to show the nature of interactions between its components like atoms/ions or lattice defects. Examination of polycrystals under pressure using diffraction methods is a well established technique. For polycrystalline materials high pressure studies are dedicated to studies on phase transformation, measurements of physical parameters like compressibility, characterization of microstructural behaviour like deviatoric stresses, *micro*-strains, yield strength, etc.

A tentative model of a nanocrystal assumes that it has a non-homogeneous structure and in this case the problem which we face is whether high-pressure diffraction technique might serve for determination of different elastic properties of inner and surface parts of the nanocrystalline grains. Obviously elastic properties are directly correlated with length of the atomic bonds which in case of nanocrystalline materials are different in the interior and at the surface of the grains. Therefore we attempt to find out if there are any specific properties of these materials which are dependent on, and correlated with, (1) the grain dimensions and, (2) the surface of the crystallites. For "ordinary polycrystals" both such effects can be ignored, but may be significant in nanocrystalline materials. In the analysis of the lattice compression one finds, that the lattice parameters determined from the positions of Bragg reflections do not have the usual meaning of a constant (the same value obtained from any Bragg reflection). Because a nanocrystalline specie constitutes a one- or two-phase (core-shell) grain, there is an obvious uncertainty as to the real meaning of the measured values of the (apparent) lattice parameters as determined from the Bragg reflections. This causes that evaluation of the elastic properties of nanocrystals requires a new approach. In this work we attempt to determine the type of the real structure of nanocrystals in comparison with conventional polycrystalline samples. We conclude that nanocrystalline samples should be characterized by two moduli (that of the core and that of the shell). Similar dilemma concerns the yield strength of nanocrystals.

Application of *in situ* high pressure powder diffraction technique for examination of specific structural properties of nanocrystals will be demonstrated for nanocrystalline powders of diamond and SiC having the average grains dimension from several to several tens of nm in diameter. Limitations and capabilities of the experimental techniques themselves and methods of diffraction data elaboration applied to nanocrystals with very small dimensions (< 30 nm) will be discussed. High-pressure in situ diffraction experiments to which we will refer to were performed in DAC at Station F3 under the pressure of up to 40 GPa. The high pressure, high temperature experiments were performed in the six-anvil cubic press MAX80 at Station F2.1, HASYLAB at DESY, Hamburg. The measurements of *micro*- and *macro*-strains were performed for dry powders and in different pressure media.

References

B. Palosz, S. Stelmakh, E. Grzanka, S. Gierlotka, R. Pielaszek, U. Bismayer, S. Werner, and W. Palosz, "High Pressure X-ray Diffraction Studies on Nanocrystalline Materials", *J. Phys.: Condens. Matter* **16** (2004) S353-S377.

C. Pantea, J. Zhang, J. Qian, Y. Zhao, A. Migliori, E. Grzanka, B. Palosz, Y. Wang, T.W. Zerda, H. Liu, Y. Ding, P.W. Stephens and C.E. Botez, "Nano-Diamond compressibility at pressures up to 85 GPa", *Technical Proceedings of the 2006 Nanotechnology Conference and Trade Show, Volume 1*.

Jianzhong Zhang, Yusheng Zhao, Bogdan Palosz, "Comparative studies of compressibility between nanocrystalline and bulk nickel", *Appl. Phys. Lett.* **90**, 043112 (2007)

Effect of thermal atomic vibrations on total and characteristic Bragg scattering of nanocrystalline materials (1h)

Bogdan PALOSZ

Institute of High Pressure Physics, Polish Academy of Sciences

Equilibrium conditions in nano-crystalline phases are different than those in large volume samples of the same composition. Also, physical properties of nanomaterials may deviate significantly from those in the bulk materials. Undoubtedly, a nano-crystal cannot be considered as a fragment of a larger size solid: it is a unique piece of matter with the properties specific for this individual object. In a tentative model, a nanocrystal is a sort of a two-phase system formed by the grain core and the surface shell, both having their own characteristic dimensions. Determination of thermal expansion coefficients (anharmonic thermal motions) and atomic temperature factors B (harmonic motions) for crystalline materials is a routine task. Neither of these parameters can be determined for a nanocrystalline material based on a conventional diffraction experiment.

Information on the effect of thermal vibrations on the scattered intensity is contained in Bragg intensities, but the same information is contained also in Thermal Diffuse Scattering (TDS), which in a conventional elaboration of powder diffraction data is disregarded. To determine atomic thermal vibration amplitudes there is widely used Wilson method which is based on examination of attenuation of Bragg intensities with an increase of temperature. The alternate approach which we propose is based on a simultaneous (coupled) examination of Wilson plots and TDS intensities. *Accounting for (examination of) TDS scattering for complex structures is not an alternative to the Wilson method but a necessity which has to be a part of the basic elaboration procedure.*

The Wilson method was originally proposed for monoatomic structures, for which atomic temperature factor is identical with the "overall temperature factor". Only for such structures the Wilson method yields unquestionable results. For polycrystalline materials with complex structures containing atoms vibrating with different amplitudes, like in nanocrystals, direct application of Wilson method might be questioned (Wilson plot is no longer a straight line with a unique slope but, it is a combination of several linear functions). Determination of the atomic temperature factors of such complex structures requires a simultaneous analysis of attenuation of the Bragg intensities and Thermal Diffuse Scattering in a large diffraction vector range. However, the unique interpretation of Wilson plots for crystals with weak vibration component(s) requires measurements performed up to a very large diffraction vector Q, ($> 25 \text{ \AA}^{-1}$), larger for weaker vibrating atoms.

For nanocrystalline SiC and diamond two different temperature atomic factors which describe vibrations of the atoms in the grain interior (B_{core}) and at its surface (B_{shell}) were determined experimentally. In situ measurements were performed at LANSCE with HIPPO (from RT up to 1100°C) and NPDF (from 15 K up to 225 °C) instruments. Atomic vibrations were evaluated based on the diffractograms calculated for models built assuming different mean square atomic displacements (vibration amplitudes) of the component atoms. Differences between atomic vibrations in powders and nano-ceramics of diamond and SiC sintered under high-temperature high-pressures conditions, which are related to transformation of free surfaces into grain boundaries, will be discussed.

References

- S. Stelmakh, E. Grzanka, Y. Zhao, W. Palosz, B. Palosz, „Neutron diffraction studiem of the atomie vibrations of bulk and surface atoms of nanocrystalline SiC”, *Zeitschrift fur Kristallographie, Suppl.* 23 (2006), 331-336.
- S. Stelmakh, E. Grzanka, M. Wojdyr, Th. Proffen, S.C. Vogel, T.W. Zerda, W. Palosz, B. Palosz, "Neutron diffraction studies of the atomic vibrations in complex materials: application of the Wilson method to examination of micro- and nano-crystalline SiC", *Z. Kristallogr.* 222 (2007) 174 - 185.