In situ nanopowder diffraction – between Bragg and diffuse scattering

Z. Kaszkur[1]* and I. Smirnov[2]

[1]*Institute of Physical Chemistry, Warszawa 01-224, Poland*
[2]*University of Warsaw, Faculty of Chemistry, Warszawa 02-093, Poland*

*e-mail: zkaszkur@ichf.edu.pl

TH_I1

Structural study of matter between amorphous and crystalline state requires approaches evolving from Debye formula as the surface cannot be treated as the phase. Nanocrystalline solids may exhibit attractive properties due to quantum confinement and extended surface. They affects thermodynamics ruled by high thermal fluctuations and surface energy. No wonder that their properties can be revealed the best via chemical interaction with the surface, in situ. The method developed by us monitors morphology of a nanopowder via diffraction addressing subtle evolution of peak positions, intensities, widths etc. during physico-chemical processes, interpreted via atomistic simulations. It provides many surprizing observations helping to understand complex processes going on. For the technique, crucial is excellent repeatability of peak position achievable (down to 10^{-4} deg), enabling interpretation of small changes regardless of limited accuracy.

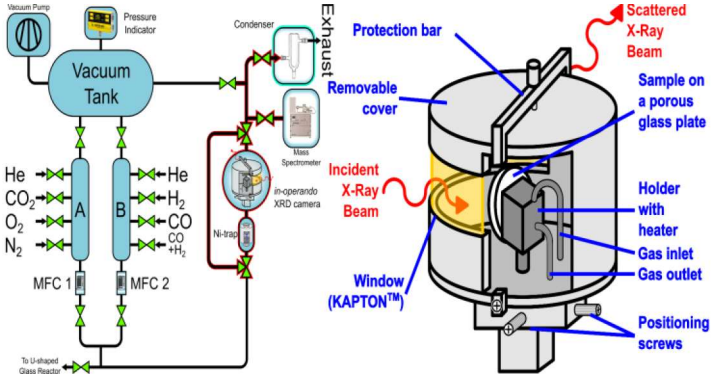

Figure 2: Scheme of experimental setup and of PXRD environmental chamber.

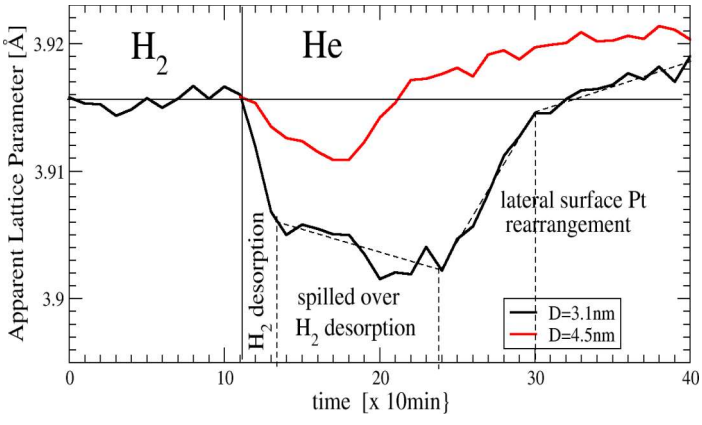

Figure 1: Evolution of ALP of Pt nanocrystal on desorption of hydrogen slowed down by reverse spill over phenomenon to last more than 5

The method addresses specific fingerprints of phenomena allowing their detection and analysis instead of global model fitting in both: real and reciprocal spaces, that tends to smear out crucial marks (like in PDF or Rietveld full profile methods). Examples presented include nanometal relaxation [1], monitoring chemisorption phenomena [2], surface reconstruction (fig.2) [3] or surface segregation kinetics in binary alloys [4]. E.g. complex phenomena of rough reconstruction of the surface of Pt nanocrystals in NO atmosphere are responsible for a low temperature coalescence of Pt [5]. Long -run monitoring of surface segregation in PdAg alloy shows segregation of Ag in He atmosphere and markedly slower segregation of Pd in CO atmosphere. This repeatable process reveals different mechanism of diffusion in both cases when in the second, CO bonds and captures Pd at the surface, hinders surface diffusion and creation of vacancies responsible for the most effective bulk diffusion mechanism (fig.3) [4].

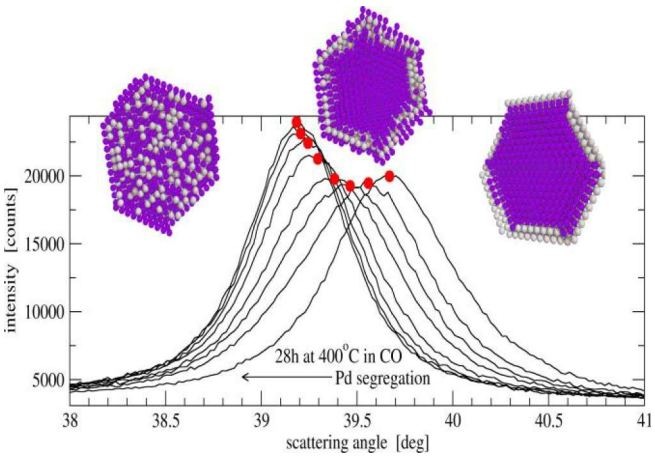

Figure 3: Evolution of 111 XRD peak of PdAg alloy during surface segregation process.

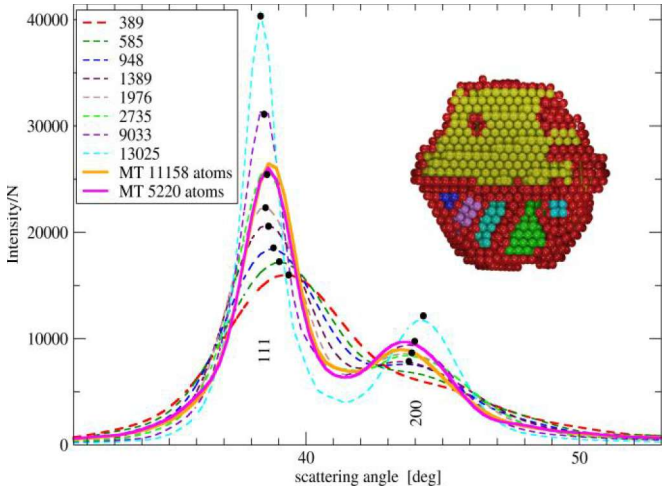

Figure 4: 111 and 200 peaks of diffraction patterns (Cu Kα radiation)for a range of Marks' decahedra. Intensity is divided by the number ofatoms. The numbers of model atoms are given in the legend. For comparison added are diffraction patterns calculated for the model of randomly multitwinned (MT) cluster consisting of 11158 atoms

The method allows insight into stacking faults occureence in FCC nanocrystals. As the energy difference between the three possible 111 plane arrangements is low, many chemicaly synthesized nanocrystals have complex domain structure consisting of locally twinned domains. It can be seen by the oversized 111 peak and slight shifts of 111 and 200 peaks. Although already noted by Warren in 1960-ties, the phenomenon can be modelled by us and the average number of domains deduced [6]. Evolution of this subtle structure can be monitored during temperature program and was observed for nanoalloys of non-miscible in bulk alloy PtAu [7].

Most of the observed processes can be modelled using designed and written by us suite of procedures CLUSTER [8] enabling graphical model building, constrained relaxation, dynamics (MD) or configurational minimization (Monte Carlo). Simulations for metals employ n-body pseudopotentials after Sutton&Chen [9].

Acknowledgements: This project was financed by a range of grants from the Natrional Science Center, Poland.

References

1. Z.Kaszkur, I.Smirnov, https://arxiv.org/pdf/2212.06926
2. P. Rzeszotarski, Z,. Kaszkur, Phys.Chem.Chem.Phys. 11 (2009) 5416–5421.
3. Z. Kaszkur, P. Rzeszotarski, and W. JuszczykJ, Appl.Cryst.47 (2014) 2069–2077.
4. Z. Kaszkur, W. Juszczyk., and D. Lomot., Phys.Chem.Chem.Phys. 17 (2015) 28250–28255.
5. Z. Kaszkur, B. Mierzwa, W. Juszczyk, P. Rzeszotarski, and D. Lomot., RSC Adv. 4 (2014) 14758–14765.
6. I. Smirnov, Z.Kaszkur, A.Hoell, Nanoscale, 15 (2023) 8633.
7. I.Smirnow, Thesis, https://rcin.org.pl/dlibra/publication/275347/edition/239362/content
8. Z.Kaszkur, B.Mierzwa, program CLUSTER, https://kaszkur.net.pl/index.php/cluster/
9. A.P. Sutton, J. Chen. Phil. Mag. Lett., 61 (1990) 139–146.