

[1] D.K. Smith, *Powder Diffraction* **1998**, 13, P.2–19. [2] A. Ilieva, B. Mihailova, Z. Tsintsov, O. Petrov, *American Mineralogist* **2007**, 92, 1325–1333. [3] E. Fritsch, *European Journal of Mineralogy* **2004**, 16, 743–752. [4] J. Pense *Zeitschrift Deutsche Gesellschaft Edelsteinkunde*. **1964**, 50, 25–29.

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In situ investigation of aragonite formation in atomic resolution by FM-AFM

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The crystallization by the interaction between organic materials and inorganic minerals is called “biomineralization”. The formation of bivalve shell is a biomineralization of calcium carbonate (CaCO₃) crystal. Some kinds of bivalve shell consist of calcite and aragonite which are polymorphs of CaCO₃ crystal. Although aragonite is metastable at normal temperature and pressure, some mollusks make aragonite stable by organic matrices [1], [2]. Amino acid sequences of some special proteins were revealed which are contained in the organic matrices of the shell, and it was confirmed that many aspartic acids are included in the proteins [3], [4].

In this study, we carried out in situ observation of aragonite formation by addition of the synthetic polypeptide which consisted of 15 amino acid residues and had periodic arrangement of six aspartic acids [3].

First of all, supersaturated solution of CaCO₃ with the synthetic polypeptide and magnesium ($\sigma=0.86$, $[Mg^{2+}]=0.05$ M, the concentration of the polypeptide = 50 μ g/ml) was loaded on the calcite crystal which was cleaved on (10-14) face, then the surface was observed in atomic level. In order to observe the change of the surface pattern in atomic resolution, *in situ* and in solution, the Frequency Modulation Atomic Force Microscopy (FM-AFM) was employed. In this solution, we succeeded to observe the moment of aragonite formation at 90 minutes after the solution was loaded. The boundary of the atomic patterns of calcite and aragonite was observed in 10 nm², and aragonite and calcite were in the same layer.

Secondly, the concentration of the synthetic polypeptide was lowered to 30 μ g/ml. In this solution, some adsorbents were observed on only calcite surface, and they adsorbed along calcium sequence of calcite [010]. The length of adsorbents is 3 - 6 nm. This is close to the length of monomolecular of the synthetic polypeptide.

These results show that calcite transforms to aragonite in the surface layer of seed crystal, and the adsorbents are likely to be the synthetic polypeptide, because aspartic acids in the synthetic polypeptide can bond to calcium atoms on the surface by carboxyl group.

Our results strongly suggest the new model of aragonite formation under normal condition by the transformation.

[1] G. Falini, S. Albeck, S. Weiner, L. Addadi, *Science* **1996**, 271, 67–69. [2] A.M. Belcher, X.H. Wu, R.J. Christensen, P.K. Hansma, G.D. Stucky, D.E. Moese, *Nature* **1996**, 381, 56–58. [3] R. Takagi and T. Miyashita, *Zoological Science* **2010**, 27, 416–426. [4] M. Suzuki, K. Saruwatari, T. Kogure, Y. Yamamoto, T. Nishimura, T. Kato, H. Nagasawa, *Science* **2009**, 325, 1388–1390.

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Quick Pt nanocrystal growth and coalescence on exposition to NO

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The morphology of Pt nanocrystals (10% wt., initial crystallite size approx. 3nm) supported on amorphous silica was studied via in situ XRD during treatment at normal pressure in He, H₂, O₂ and NO. A specially designed experiment and its analysis enabled detecting of subtle changes in XRD pattern that could be interpreted via atomistic simulations. At the same time a composition of the gas phase could be monitored via Mass Spectrometry (MS). Evolution of Pt fcc peaks position, intensity and width proved to be sensitive to a surface effect and we were able to observe and analyze surface reconstruction of Pt nanocrystals on exposition from H₂ to He [1]. On exposition to NO at temperature 100°C we observe a relatively quick (in a few hours) Pt crystallite growth process. As a result a distribution of an ordered atom column length (closely related to the crystallite size) becomes evidently bimodal with mode size ~3.4nm and ~16.8nm (from 111 reflection). Qualitative analysis (Williamson-Hall plot) revealed only small contribution of microstrain to the peak broadening. Analysis of three reflections 111, 200 and 220 suggests crystal growth process to be anisotropic with preferential growth in 111 direction. During this process MS reveals evolution of N₂, O₂ and some amount of N₂O with changing rate (the latter present also in a supplying gas pressure bottle).

A precise analysis shows that the peak position also evolves anisotropically during the growth process. For nanoparticles Bragg law is no longer obeyed precisely and the peak position does not point to the interlayer distance [2,3]. The peak position depends on the crystallites size and on the state of its surface evolving with surface relaxation (and chemisorption phenomena). This also results in a slightly shifted contributions to the peak profile originating from smaller and larger atomic column lengths. Such dependence of a peak position with the crystal size makes classical analysis using Warren-Averbach approach very difficult and sometimes misleading [4].

The observed quick growth of Pt nanocrystals slows down and stops after few hours and the most likely mechanism is coalescence of larger crystallites swallowing the smaller neighbors.

[1] P. Rzeszutowski, Z. Kaszukur, *Physical Chemistry Chemical Physics* **2009**, 11, 5416–5421. [2] Z. Kaszukur, *Journal of Applied Crystallography* **2000**, 33, 87–94. [3] Z. Kaszukur, *Zeitschrift für Kristallographie* **2006**, 23, 147–154. [4] Z. Kaszukur, *Journal of Applied Crystallography* **2005**, 38, 266–273.

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Synthesis of Nd-Fe-B nanocomposite magnets by reactive mechanical milling

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Nd-Fe-B nanocomposite magnets composed of a Nd₂Fe₁₄B hard magnetic phase and soft magnetic phases such as α -Fe and/or Fe-B compounds are known to exhibit excellent magnetic properties due to strong ferromagnetic coupling between the magnetic phases [1]. Hydrogenation-decomposition-desorption-recombination (HDDR)