In situ observation of formation of bimetallic PdOs nanoalloy during thermal decomposition a single-course precursor $[Pd(NH_3)_4][OsCl_6]$

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A double complex salt $[Pd(NH_3)_4][OsCl_6]$ with orthorhombic *Cmca* structure has been considered as a precursor for preparing bimetallic nanoalloys. A binary phase diagram of Pd-Os is a peritectic type with solubility of bulk Pd and Os of around 3at.% in the temperature range of 20-1640º C. This suggests two types of nanoalloys: one is based on *fcc*-Pd, and the other, *hcp*-Os. One believes that mixing metals on atomic level in double complex salt promotes a formation of nanoalloy, which can not be existed in bulk. Indeed, PtOs nanoalloy was found to form in a process of thermal decomposition of $[Pd(NH_3)_4][OsCl_6]$ in an inert atmosphere despite on poor solubility similar to $[Pd(NH_3)_4][OsCl_6]$. To follow a process of the PdOs nanoalloy formation through thermal decomposition of $[Pd(NH_3)_4][OsCl_6]$ in the inert atmosphere, *in situ* combined XAFS at Pd K- and Os L_3-edges, X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (PXRD) study have been performed.

XAFS experiment was carried out in transmission mode on PAL at 10C beamline of PAL POSTECH (Pohang, South Korea). PXRD experiment was performed at the Swiss-Norwegian Beam Line (BM01A, at the ESRF). XPS spectra were measured on a Phoibos 150 SPECS spectrometer using MgKα radiation (1253.6 eV).

A two-step mechanism of thermal decomposition of $[Pd(NH_3)_4][OsCl_6]$ was found. In contrast to other similar complex salts such as $[Pd(NH_3)_4][PtCl_6]$, $[Pd(NH_3)_4][IrCl_6]$, in case of $[Pd(NH_3)_4][OsCl_6]$ each step deals with the formation of nanoalloy. At the first step, reducing Pd(II) to Pd(0) is accompanied by a formation of monometallic Pd nanoparticles (250ºC). At the second step, Os(IV) reduces to Os(0) and Pd_{core}-Os_{shell} and Os_{core}-Pd_{shell} are formed around 320ºC. A further increase in temperature (up to 500ºC) results in the formation of nanoalloy, when atomic ordering has been changing. This process is finished only after cooling. The final product is a heterogeneous multicomponent system, which can be described as a mixture of *fcc*-Pd, *hcp*-Os, *fcc*-Pd_xOs_{1-x} and *hcp*-Os_yPd_{1-y} (x and y > 0.8).

Unusual behavior of the Os L_3-edge EXAFS spectrum is observed in a far *k*-range under high temperature (above 370 ºC). A special approach in treatment of EXAFS spectra allows a contribution from metallic Os clusters to reveal.

XANES and EXAFS data will be supplemented with PXRD and XPS data.

In situ combined XAFS, XPS and PXRD study showed that the heterogeneous multicomponent system consisted of PdOs nanoalloy and monometallic Pd, Os particles is formed in a process of thermal decomposition of $[Pd(NH_3)_4][OsCl_6]$ in two steps.

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