Nanocomposites and nanomaterials

Probing sub-atomic free-volume imperfections in wet-milled nanoarsenicals with PAL spectroscopy

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Nanostructurization effects were probed in arsenic sulfide composites with complementary atomic-specific (X-ray diffraction, Raman scattering and scanning electron microscopy) and atomic-deficient (positron annihilation lifetime – PAL) techniques allowing reliable identification of products formed under high-energy wet milling. The starting materials for mechanosynthesis were arsenicals such as realgar As_4S_4 polymorphs (- and -phase, pararealgar) and $As_{55}S_{45}$ alloys crystallized in a mixture of realgar As_4S_4 and dimorphite As_4S_3 phases, the 0.5 % polyvinylpyrrolidone (PVP) water solution being used as nonionic stabilizer. It was shown that palletized nanoarsenicals were in strong relation to coarse counterparts used for nanomilling with surface extraction of arsenilite As_2O_3 crystallites.

The PAL data were treated within algorithm of mixed substitutional trapping, describing transformation of positronium sites in pure PVP matrix into positron trapping sites in nanoparticle-modified matrix [1]. Interfacial free-volume voids of sub-atomic sizes created by neighboring arsenical nanoparticles embedded in PVP environment were defined as most efficient positron traps, they being rather loosely composed by few nanocrystallites in full respect to crystallographic data. These annihilation channels were preferentially related to intrinsic free-volume voids, which were insensitive to positron trapping states at the surface of oxidized pellets. Observed compositional variations in mixed positron-positronium trapping modes were adequately explained in respect to the chemistry of the nanoarsenicals.

1. *Shpotyuk O., Filipecki J., Ingram A., et al*. Positronics of subnanometer atomistic imperfections in solids as a high-informative structure characterization tool // Nanoscale Res. Lett.-2015-10-P. 77-1-77-5.