FORMATION OF MULTI PHASE NANOSYSTEMS DURING SOLID STATE TRANSFORMATIONS AND REACTIONS AT VARIABLE P,T,PO_2, PH_2O

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Nanosystems are defined as the systems consisted of nanoparticles, namely of particles of $10^{-9} – 10^{-7}$ *m* in size. Nanoparticle can be nano sized in either one, or two or three dimensions in dependence on the habitus described as the film (or lamella, or plate), the needle and the sphere correspondingly. Nanosystems can be formed by crystallization (condesation) processes as well due to solid state transformations in massive solid (in "host mineral") [1]. That minerals which have nano sized areas of either different chemical composition, or different structure or different orientation and, thus, have internal boundaries between these areas such as interface boundaries, twinning planes, planar defects, domain boundaries, are considered as nanosystems. Nanosystems are characterized by a large free surface and, consequently, by a high surface free energy. The contribution of surface free energy to bulk free energy results in the change of physical, thermodynamic and reactivity properties of nanosystems with respect to macrosystems [1-3].

Solid state transformations and solid state reactions proceed in a mineral due to a change in physico-chemical parameters. As a result, new nano sized phases are nucleated in crystalline matrix and thus initially homogenious (single phase) macrosystem transforms into multi phase nanosystem. Coherent interfaces are formed in a crystal and thus elastic strains arise. Elastic strain energy contributes to the bulk free energy resulting in a shift of equilibrium for nanosystem relative to macrosystem and making possible a stabilization of metastable states ("forced equillibria" [2,3]). As a result, inclusions of high pressure phases are conserved in a host mineral during the decompression; metastable phases and phase associations forbidden at given P-T conditions appear; cation-deficient phases with the crystal structure of the host mineral appear instead of equilibrium products of transformation. At a phase diagram this leads to a depression of solvus (a coherent solvus appears); to a shift of *P-T* boundaries of polymorphic transitions; to a substitution of equilibrium stability fields by metastable equilibrium fields (phase size effect [2,3]).

Multi phase nanosystem formation features were considered for solid state transformations (exsolution, polymorphic transitions) in TiO_2-SnO_2 system at high *P-T* [4] as well as for solid state reactions of oxidation and hydration (protonization) of olivine [5-8]. The available data allow make some conclusions concerning the macro- to nanostate transition:

(1) Formation of nanosystems is accompanied by the appearance of coherent phase interfaces.

(2) Nanosystems formed during the oxidation or hydration processes are characterized by appearence of cation-deficient vacancy-bearing nanophases with the crystal structure similar to the crystal structure of the host phase. The examples of such cation-deficient nanophases are hydroolivine $(Mg_2SiO_4)n(MgH_2SiO_4)$ and laihunite $(Mg,Fe^{2+})_{2-3x}Fe^{3+}_{2x}SiO_4$ precipitations in olivine.

(3) Polysynthetic twinning is a typical mechanism of the nanosystem formation during polymorphic phase transitions (α-γ polymorphic transition in TiO_2, clino-orthopyroxene transition etc.).

(4) Nanophases are stabilized by the crystal lattice of the host mineral due to the elastic strain energy of coherent interfaces and are metastably conserved under variable P,T,PO_2, PH_2O. The examples of such "forced eqiulibria" are the conservation of high-pressure nanophases in the crystal matrix of the host mineral at the normal *P-T* parameters (lamella of γ-TiO_2 in α-TiO2 (rutile) and the exsolution of hydroolivine in olivine).

(5) The nanosystem formation during solid state transformations and solid state reactions is facilitated by supersaturation conditions and low rates of diffusion (low temperatures); by high PO_2 and/or high PH_2O at low temperatures; by rapid quenching.

(6) A role of the pressure in the nanosystem formation processes is not well known. However, even few in a number available data suggest that a behavior of nanosystems and macrosystems at high pressure is different. The new high pressure cation-deficient phase – hydroolivine – found as nanoprecipitates in mantle olivines [7] suggests the high pressure exsolution process for its formation. There can be little doubt that during the following decompression the hydroolivine nanoinclusions were metastably conserved by the crystal lattice of the host olivine due to elastic strain force. As a result, the high pressure phase hydroolivine is metastably conserved at low external pressures, whereas the serpentine + talc assemblage is equilibrium at low-pressure conditions in the MgO-SiO_2-H_2O macrosystem. Compared to macrosystem, the α-γ TiO_2 polymorphic transition occurs in nanosystem at lower pressures [4]. Experimental data on the pressure effect on the solvus position for TiO_2-SnO_2 solid solutions show a depression of the solvus at increased pressure. The critical temperature of solvus is 1430 ^{o}C (1 atm), <1320 ^{o}C (2.5 GPa), <1230 ^{o}C (3.5 GPa), <1200 ^{o}C (4.5 GPa) and <1150 ^{o}C (5.5 GPa). Such a behavior of solid solution is completely contradictory to the equilibrium thermodynamics of macrosystems as well as to the theory of isomorphous solubility [9], which both predict that the critical temperature of solvus is to be increased as the pressure increases. Such unusual behavior can be explained by a phase size effect. When we suppose that the surface energy should increase as the pressure increases, the depression of solvus is to be expected. At the same time, at high pressures the macro- to nanostate transition would occur at larger critical size. This means that the behavior typical for nanosystems can be exhibited for significantly more large particle size at high pressures than at normal pressure.

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