

Comparative analysis of thermoscale effects, isomerization and stability of TM-nanoclusters (Pd,Ni,Fe) and Si in dependence on interatomic potentials. MD-simulations

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Abstract. Basing on the MD-simulated data the comparison of physicochemical properties of TM-nanoclusters (Pd,Ni,Fe), and Si-nanoparticles has been carried on in the purpose to understand the specificity of structure changes in depending on nature of interatomic bonds and initial structures (fcc, bcc, icosahedral – Ih). MD-simulation of thermic evolution including melting of TM- and Si- clusters was carried on up to 2000K.

1. Introduction

The comparative analysis of structure-isomeric transitions and the thermostability of nanoclusters (“quantum dots” about 2-5nm sizes and with number of atoms up to several hundreds) transition-metal – (TM₅₅₋₅₆₁: Ni, Pd, Fe) and ones with covalent bonds, such as Si-clusters and its hydrides has been carried out in dependence on the initial cluster structures at the heat treatment and melting. For this purposes MD simulation with correctly parameterized functions of Sutton-Chen potential for transition metal atom interactions and for silicon atoms—a coordination potential of Tersoff were delivered accurately and in detail. The variable structures were represented by crystalline types – bcc, fcc and non-crystalline one – aperiodic, icosahedral for Ni but amorphous, glasslike ones contained from 300 to 500 atoms, nanoassembler, obtained either by intercalation of 13 atomic icosahedron into 60 atomic fullerene-like spheroid for silicon systems or by H-passivation (H₆₀Si₆₀).

2. TM clusters and thermoscale effects

The most implication of nanodispersed states (nanocluster one including) of transition metal (TM) powders in condition of precision mass spectrometer calibration of sizes and forms is manufacturing as high effective catalyzers, so information carriers in forms 2D groups (2D-spacers) of nanoclusters immobilized on dielectric substrates. The using of TM-nanoclusters, as cooperative catalyzers is more productive in the processes of de- and hydrogenation in comparison with conventional ones. According with well known experimental practice the optimal sizes of catalytic TM-nanoclusters have the strict limits, namely, from 1,2nm to 2,0nm correlating with ones of perfect icosahedral (Ih), cube octahedral (fcc) forms of Me-nanoclusters containing magic number 147-561 atoms of Cini series (Me₁₄₇₋₅₆₁). Taking in account the actuality and importance of problem and large body of systematic researches and experimental data concerning thermoscale effects, however much has yet to be learned about specific thermodynamics of phase transitions in nanoscale (structure isomeric changes of

premelting, melting as itself and crystallization)[1]. Using the accurate optimized potential functions [2] MD simulation of thermic evolutions of Cini series TM-nanoclusters (TM₁₃₋₅₆₁: Ni, Pd, Rh) has been carried on and the thermodynamic data have been obtained in dependence on the initial nanocluster coordinations (fcc, bcc or Ih). We have analyzed the received data in nanoscale and revealed the nature of melting, as many stage process (isomerization, “quasimelting” with coexistence of fluidlike upper shells and solid of inner ones) and freezing stages under cooling - nucleation, cluster growth with consequent layer-by-layer its perfect shells forming space extent structures. By using the obtained information about nanocluster configurations the reconstruction of possible ways of their self-adjusting and mutual spacing on the dielectric substrate surfaces in the process of formation of designed periodical, net or amorphous structures of “2D-spacer” catalyzers have been delivered. Analyzing the obtained data of computers simulation of thermic cluster evolutions it was revealed that thermoscale effects of TM-nanosystems under heating and cooling have been manifested not only by essential lowering of melting temperatures and broadening of temperature interval of phase transitions, but in other temperature dependant characteristics as internal stresses, pressures, anomalous behavior of heat capacity, and by such premelting effect, as isomerization with changing initial structures, mutual transitions to alternative ones (back-and-forth: fcc → Ih → bcc) and partly amorphous phase or icosahedral with appearing of vacancies and adatoms in upper shells. Thus the process of melting Ni, Pd, Fe nanoclusters was characterized broaden by temperature range of quasi stage initiated first of all with intensive diffusion interchangeable motions of atoms in surface vertices and edges. According to analysis, increasing of structure disordering has lead to disappearing shell and facet structure and affect of an opposite direction sliding, Figure 1. But central facet and inner core atoms of nanoclusters were the most motionless ones. It was significant also, that the radial and tangential self diffusion components (D_R D_T) were noticeable changed from surface shell to inner ones (for Ni₅₆₁ at 650K the

corresponded activation energies of fifth shell were $E_R = 0.28\text{eV}$; $E_\tau = 0.015\text{eV}$ and for underlaid fourth one: were $E_R = 0.41\text{eV}$; $E_\tau = 0.19\text{eV}$.

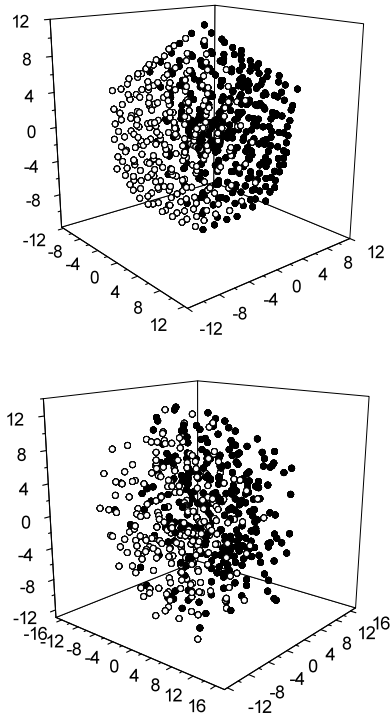


Fig. 1. Nanoclusters Ni_{561} : (top) with initial Ih-structure; (bottom) disordered one after melting.

It's an essential that with functional deposition metal clusters on substrate deposit of Ni and Pd clusters on substrates (TiO_2 , SiO_2 , MgO) stabilized the clusters with substantial rising of temperature of phase-structural transitions (as isomerisation, quasismelting etc.) and narrowing their temperature intervals. The effect is explained by taking in account the excluding from heat activated diffusion the facet atoms (about 15) contacting with supporting substrate. Moreover the motionless metal atoms on substrate caused the deceleration effect on interchange atom diffusion and tangential sliding in opposite directions of atoms of adjusting shells to conserve summary impulse of atom motions of clusters.

Thus the formations of noncrystalline hierarchic fractal clustered aggregations of Mackey "clusters of clusters" were preceded (as precursors) to crystallization of bcc, fcc phases for higher cooling rates. Basing on statistic-geometry the simulated nucleation and growth of nanophases formed with extended packs of regular and truncated tetrahedral conjugated on trigonal and pentagonal faces have been studied demonstrating the efficiency of delivered analysis of abovementioned structures not only in frame of canonical principles of Mackey globular polytetrahedral short-ordered clusters with pentafold symmetry, but on the base of alternative Ino or Friauf polyhedral conjugated on hexagonal facets and Burdiiik-Coxeter helicoidal chain meso- and long ordered nanofragments as the most strength and stable elongate coordinations in nanophases. For Pd_{561}

clusters the stable structure was formed in process of heating up to 500K of initial Ih-structure by coherent combination those distorted Ih, Ino polyhedra and hcp coordinations, Figure 2.

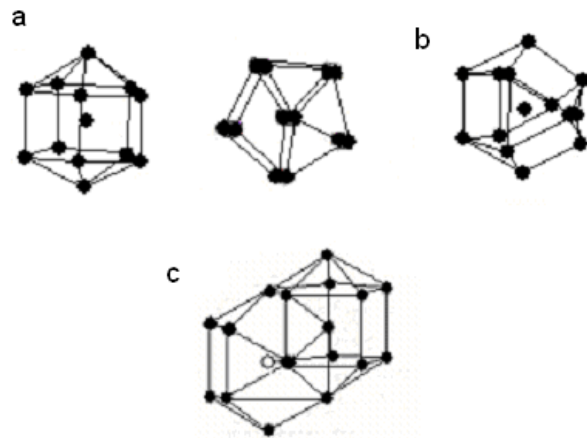


Fig. 2. Structure of Pd_{561} cluster: a) Polyhedra Ino; b) hcp; c) their combination.

3. Thermostability of Si-assembler clusters

Basing on MD-simulateion data of Si-nanoparticles, as quantum dots having excellent optoelectronic characteristics (competitive para to those of GaAs compound) the analysis of physicochemical properties has been carried out. The increasing of thermodynamic stability and retaining of functionally designed morphology are important problems for cluster serveability at high temperatures. To increase the thermostability of Si (or Ge) fullerenelike and nanotube structures at temperatures above 500K some procedures were applied such as intercalation of structure cavities with tetrahedral seeds (Ih- Si_{13}) of the same atoms or another atoms (alkaline, transition metal), hydrogen passivation of floating, dangling and broken covalent bonds. We revealed [1], that regular two shell assembling Si_{45} -clusters, obtained by intercalation of fullerene cavities with tetrahedral 3-9 atomic seeds (e.g., $\text{Si}_{45} \rightarrow \text{Si}_7@ \text{Si}_{38}$ or $\text{Si}_{45} \rightarrow \text{Si}_9@ \text{Si}_{36}$ [1]) were the most thermostable. For the most part of processes of cluster synthesis were undergoing at elevated temperatures with including phase transitions and therefore it's an actual to analyze MD-simulation data of cluster thermoevolutions–melting (premelting, structure isomerization), supercooling, nucleation. For this purpose the thermostability of noncrystalline Si-nanoparticles of 300,400, 500 atoms and assembled Si_{73} -cluster $\text{Si}_{13}@ \text{Si}_{60}$ at the heating from 300K up to 2100 have been studied in the frame of MD method using Stillinger-Weber threebody potential for tetrahedral coordinated Si particles and Tersoff coordination potential for fullerenelike Si_{73} -assembler. As it was revealed not only with increasing of atom numbers in simulated nanoclusters their thermostabilities increased but due to the perfect shell and surface structure (especially concerning of edge and vertex atoms of TM-clusters), H- passivation

($H_{60}Si_{60}$) or with intercalation of floating bonds ($Si_{13}@Si_{60}$). Such enforcing the structure of covalent bonded silicon nanoclusters was sufficient to undergo the heating up to 1640K in contrast with metal cluster Me_{561} , Figure 3.

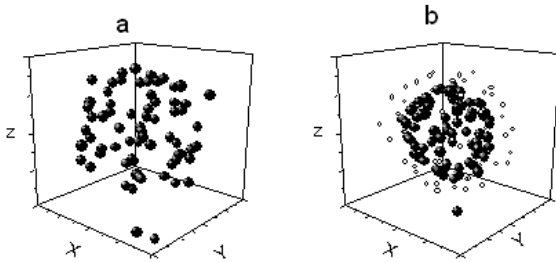


Fig. 3. Structures of silicon nanocluster: a) assembler-clusters $Si_{13}@Si_{60}$ b) ligand with hydrogen (H_{60}) shell $Si_{13}@Si_{60}:H_{60}$ at the final stage of their thermic evolution (100ps) after heating up to 1560K.

Conclusion

Thus the initial diffusion of atoms from vertex along edges was most important for starting process quasimelting and final disordering of inner coordinations and shell structure as itself. The visible evidence of melting was the rounding and distorting facet structure and then their disappearance. The deposition catalytic clusters on substrates as has been revealed increased noticeable their thermostabilities. Hydrogen ligand in the case Si assembler-clusters was stable due to H passivation of floating (free) Si-bonds and enforcing with capillary tension of inner Si_{73} cluster.

References

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- [2] Voter A. F., Chen S.P. Accurate Interatomic Potentials for Ni, Al, Ni_3Al In "Characterization of Defects in Materials" edited by R.W. Siegel, J.R. Weertman, R. Sinclair, MRS (Material Research Society) Symp. Proceeding. N.82, Pittsburg, 1987, p. 175.