ISSN 1995-0780, Nanotechnologies in Russia, 2008, Vol. 3, Nos. 11–12, pp. 691–696. © Pleiades Publishing, Ltd., 2008.
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EXPERIMENT

Quantum-Mechanical Study of Elastic Properties of Nanoparticles and Their Agglomeration Processes

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Received May 12, 2008

Abstract—The response of nanoparticles of different nature (metals, covalent materials, and oxide dielectrics) to tension, compression, and adhesion was studied using the electron density functional theory and pseudopotential methods. It was shown that the elastic modulus of nanoparticles, as a rule, exceeds the corresponding values of a bulk material by several times. Bringing together nanoparticles causes, as a rule, their spontaneous adhesion (agglomeration) accompanied by a noticeable change in the initial shape and electronic structure.

DOI: 10.1134/S1995078008110049

INTRODUCTION

One of the important fields of application of nanoparticles is powder metallurgy and other technological processes in which pressing and sintering are main operations. Moreover, such phenomena (compression and tension of nanoobjects) occur in the maintenance of nanomechanical devices whose fabrication and application are rapidly expanded. Therefore, it is necessary to know how nanoparticles respond to tension and compression and how they interact with each other. This problem is not trivial, since the atomic structure of nanoparticles is very sensitive to interactions due to their small sizes. It is clear that the behavior of nanoparticles of different nature (metals, covalent materials, and oxide dielectrics) should be different; however, quantitative results in this direction can be obtained using precision nanoscale experiments or high-accuracy quantum-mechanical calculations. This paper is devoted to the quantum-mechanical study of this problem using the electron density functional theory and pseudopotential method.

CALCULATION METHODS AND DETAILS

Aluminum (metal), silicon (covalent semiconductor), and zirconia (oxide dielectric with ionic bond) were chosen as model materials. Since spin polarization effects often appear in nanoparticles (even in the cases of nonmagnetic elements), the spin-polarization version of the electron density functional method was used (FHI96spin package [1] tried-and-true in the study of the atomic and electronic structure of metal, semiconductor, and dielectric systems, including nanoscale ones). Pseudopotentials were calculated using the FHI98pp package [2] and were tested on bulk materials. For silicon, the Hamann pseudopotential [3] was used; for aluminum, oxygen, and zirconium, the Troullier–Martins pseudopotentials [4] were used. All of these are norm-conserving and transferable. Exchange-correlation effects were calculated in the generalized gradient approach (GGA); the cutoff energy for the plane-wave basis for silicon and aluminum was 14Ry; for ZrO_2, it was 40Ry. Since the FHI96spin package is based on the periodicity principle, in all cases simulation was performed using the method of a supercell whose sizes exceed nanoparticle sizes so that the interaction between periodically translated particles is negligible. Calculations were carried out with only one (central) point of the Brillouin zone. Test calculations showed that gamma points are sufficient to provide convergence in both the energy and atomic configuration even for metal nanoparticles since they are characterized by a discrete dielectric-type electronic spectrum due to their small size. Al_2, Al_3, Al_4, Al_8, Al_{13}, Si_5, Si_{10}, Si_{18}, Zr_6O_{12}, and $Zr_{10}O_{20}$ nanoparticles were studied.

Elastic characteristics were analyzed using the technique [5], according to which the elastic modulus (Young's modulus) K can be calculated from the change in the total particle energy E during particle deformation (elongation or contraction) along a certain direction d:

$$K = \frac{\partial^2 E}{\partial d^2}\frac{d_0^2}{V_0},$$

where V_0 and d_0 are the equilibrium volume and equilibrium length of the particle. The particle volume is determined from volumes occupied by each atom separately:

$$V_A = \frac{4}{3}\pi R_A^3,$$

where R_A is the atomic radius.

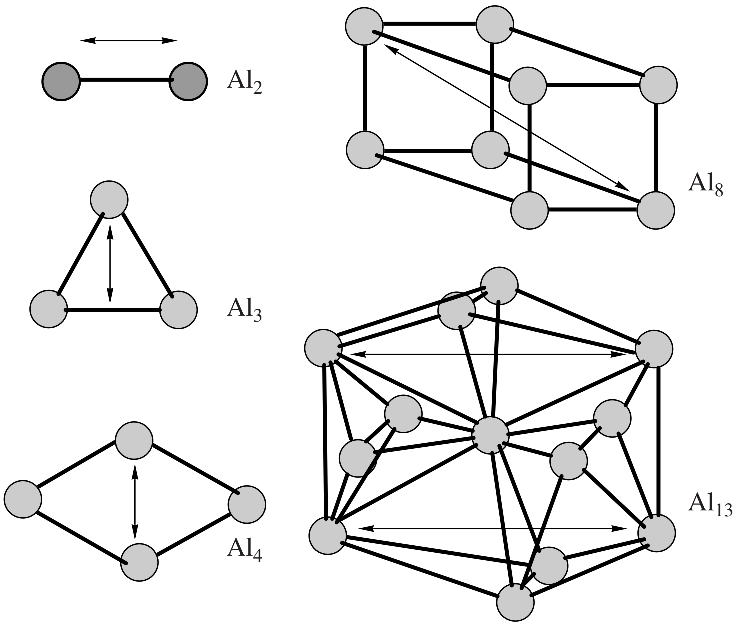

Fig. 1. Schematic representation of the aluminum nanoparticle structure.

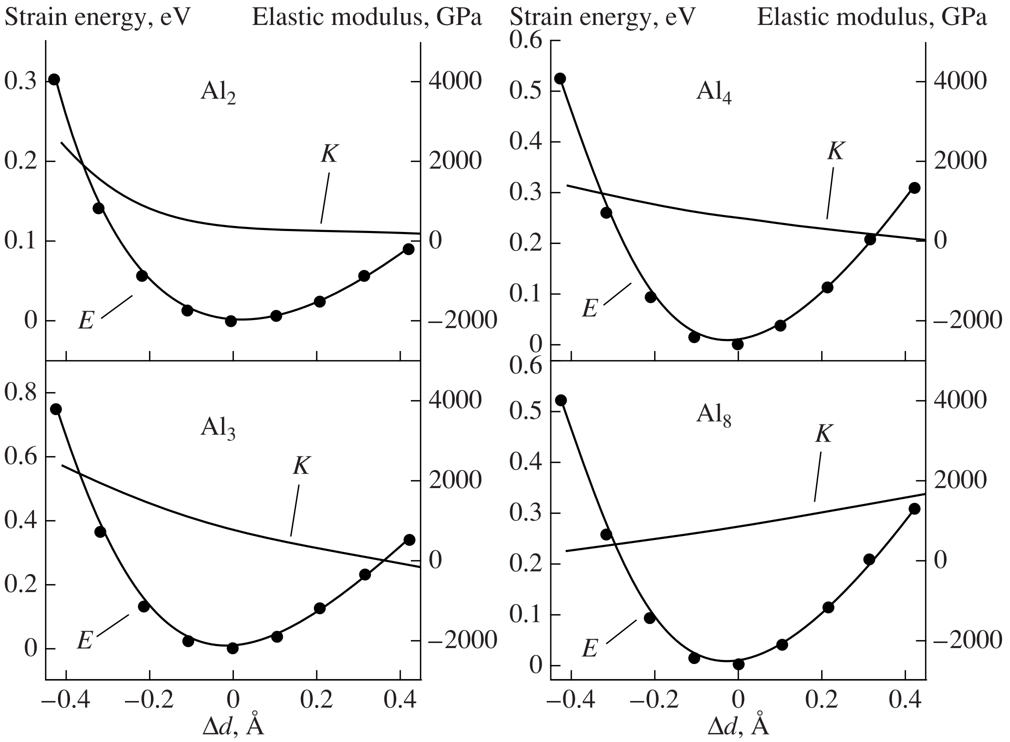

Fig. 2. Dependences of the energy E (left vertical axes) and elastic modulus K (right vertical axes) of aluminum nanoparticles on the strain Δd.

ELASTIC BEHAVIOR OF NANOPARTICLES

Calculations showed that nanoparticles with metal, covalent, and ionic bonds respond differently to mechanical deformation.

Figure 1 shows aluminum nanoparticles studied in this work. Arrows indicate the directions along which particles were subjected to tension and compression deformations. Figure 2 shows the dependences of the

Equilibrium elastic modulus K_0(nano) in comparison with the macroscopic elastic modulus K_0(macro)

	Al_2	Al_3	Al_4	Al_8	Al_{13}	Si_5	Si_{10}	Si_{18}	Zr_6O_{12}	$Zr_{10}O_{20}$
K_0(nano), GPa	230	486	342	411	296	585	342	206	572	555
K_0(macro), GPa	70					166			171–186	

energy E and elastic modulus K of aluminum nanoparticles on the strain Δd. We can see that aluminum nanoparticles cannot be considered as elastic ones in the strict sense of this word, since their elastic modulus determined through the second derivative of the strain energy is not constant even for small strains. For plane particles ($n = 2, 3, 4$), the elastic modulus increases during compression and decreases under tension. The elastic modulus of three-dimensional particles ($n = 8, 13$) behaves oppositely. Equilibrium elastic moduli K_0(nano) (corresponding to the equilibrium configuration of particles) are listed in the table.

The studied silicon nanoparticles are shown in Fig. 3. The calculated dependences of the strain energy on compression and tension are shown in Fig. 4. The equilibrium elastic moduli for silicon nanoparticles in comparison with the elastic modulus of bulk silicon are listed in the table. We can see that the elastic modulus of nanoparticles rapidly decreases with their size and already exceeds the elastic modulus of bulk silicon for the Si_{18} particle by only 24%.

To study elastic characteristics, stoichiometric Zr_6O_{12} and $Zr_{10}O_{20}$ particles (Fig. 5) with rhombic (tetragonal-like) symmetry were used as zirconia nanoparticles. The size dependences of the total energy of Zr_6O_{12} and $Zr_{10}O_{20}$ nanoparticles are shown in Fig. 6. We can see that these dependences are almost parabolas, i.e., zirconia nanoparticles behave as classical elastic particles. The table lists Young's moduli K_0(nano) of nanoparticles as a function of size in comparison with the data on the bulk material.

The literature contains experimental data on linear compressibility (1/K) of zirconia nanoparticles 18 nm in size [6]. It is 1.41×10^{-12} Pa^{-1}. For Zr_6O_{12} and $Zr_{10}O_{20}$ nanoparticles, this value is 1.75×10^{-12} and 1.80×10^{-12} Pa^{-1}, respectively. Hence, the calculated elastic characteristics are in good agreement with the experimental data for zirconia nanoparticles, despite the fact that much larger particles were studied in [6] than in the present work. As the calculations we performed show, this is probably because elastic properties of nanoparticles depend weakly on size (at least at sufficiently small sizes). At the same time, it is important that in general the elastic modulus of nanoparticles is much larger—about three times—than that of a bulk material.

NANOPARTICLE INTERACTION

Nanoparticle interactions were studied using Al_6, Al_{13}, Si_5, Si_{10}, Zr_6O_{12}, and Zr_7O_{14}. It was found that the interaction is first of all controlled by the interatomic bond type. In the case of aluminum (metal bonds), approach of particles, independently of their size, leads to their spontaneous attraction. Particles are extended toward each other, their interatomic distances increase, and they tend to contact almost without changing the initial atomic structure. The distance dependence of

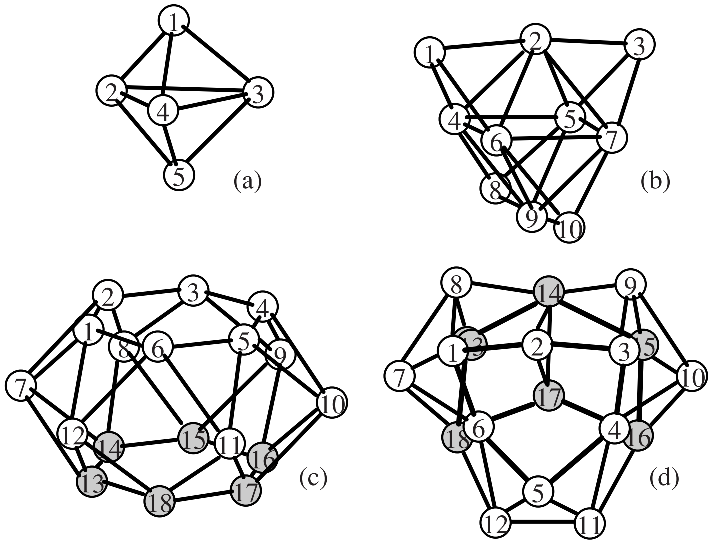

Fig. 3. Silicon nanoparticles: (a) Si_5, (b) Si_{10}, (c) Si_{18} (unrelaxed), (d) Si_{18} (relaxed, view from the side of hexagon 1–2–3–4–5–6; atoms of the lower hexagon are indicated by gray color).

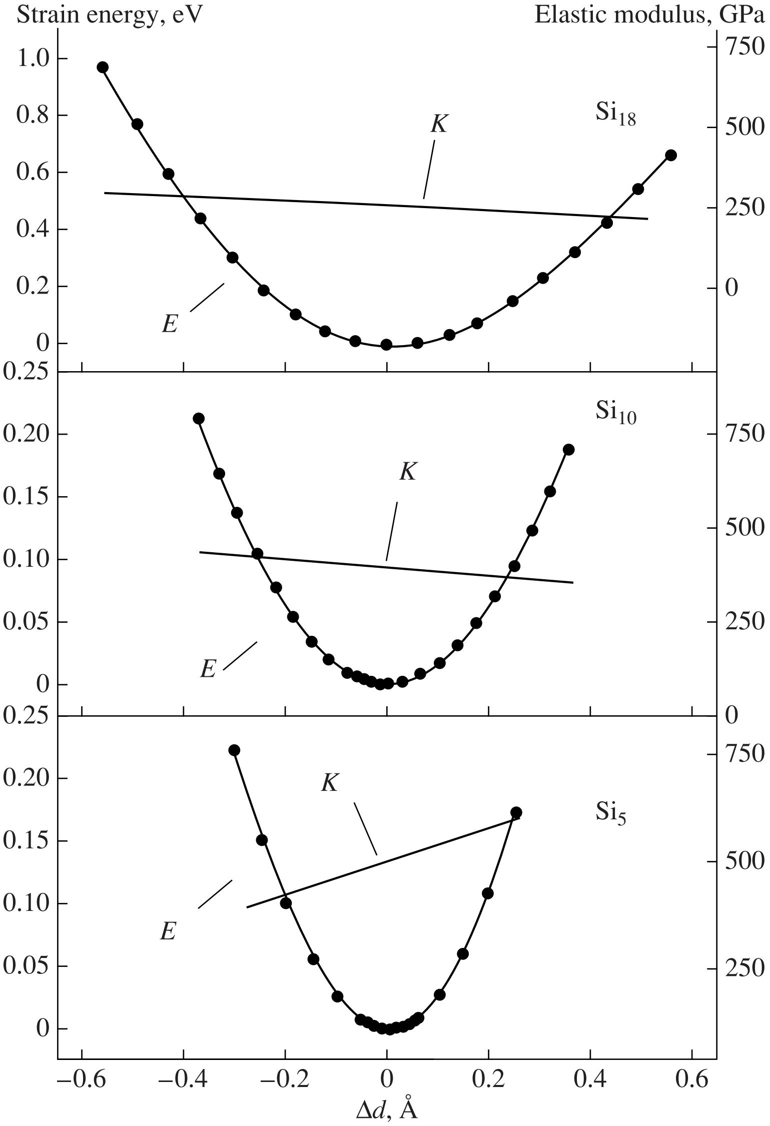

Fig. 4. Dependences of the energy *E* (left vertical axes) and elastic modulus *K* (right vertical axes) of silicon nanoparticles on the strain Δ*d*.

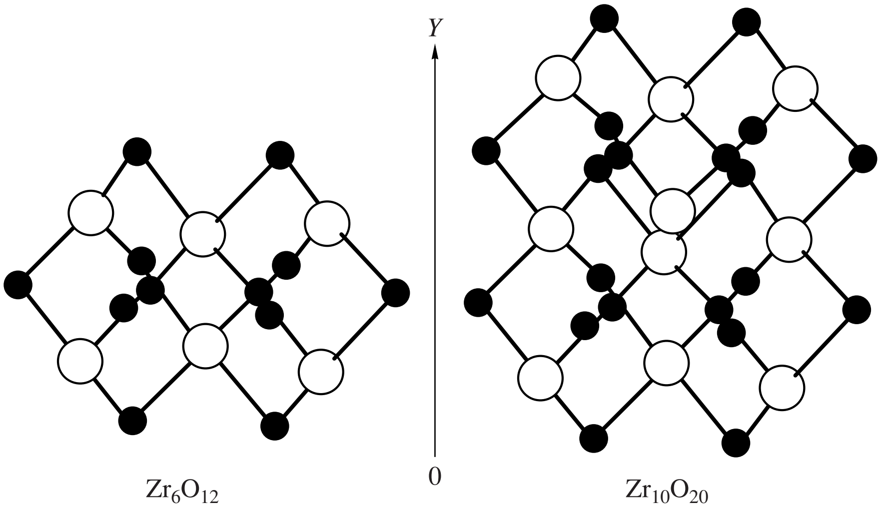

Fig. 5. Atomic arrangement in zirconia nanoparticles. Bright and dark balls are zirconium and oxygen atoms, respectively.

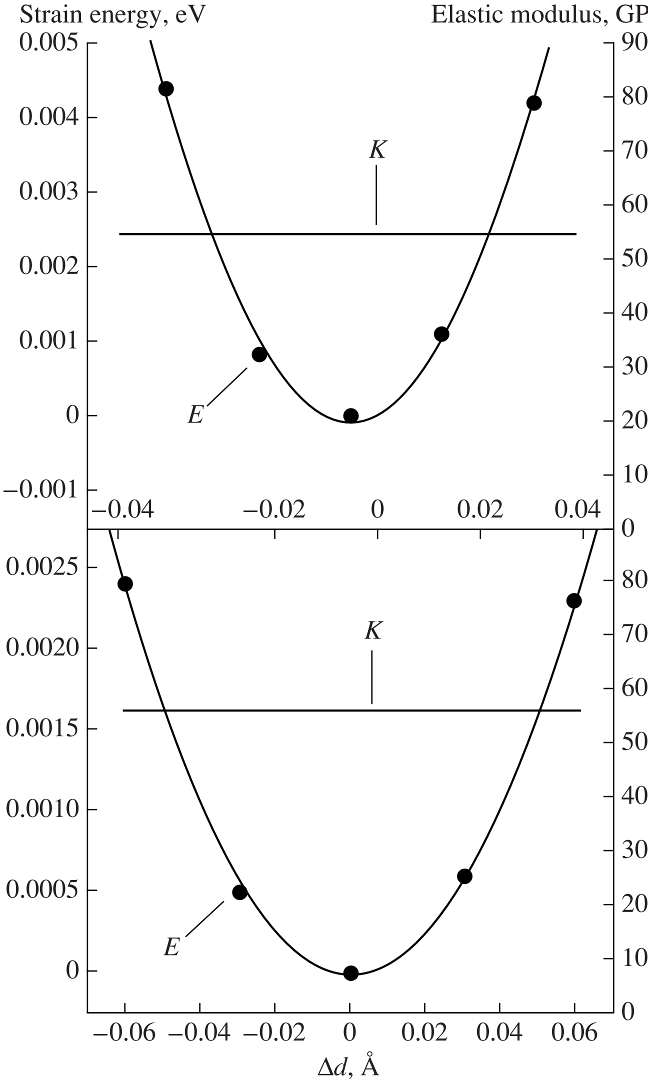

Fig. 6. Dependence of the total energy of zirconia nanoparticles on their strain Δ*d*. Horizontal lines correspond to elastic moduli.

their interaction energy is shown in Fig. 7. We can see that metal nanoparticles agglomeration is barrierless and does not require thermal or other activation.

The case of silicon is more complex. The atomic structure of nanoparticles tends to transform during the interaction to saturate covalent bonds to a maximum extent. The transformation requires breaking of some existing bonds, which results in the formation of barriers and the necessity of process activation by an external energy (e.g., temperature). Figure 8 shows the energy curve of interactions for pairs Si_5 + Si_5 and Si_{10} + Si_{10}. In the former case, the atomic structure transformation occurs rather efficiently, and particles are bound with an energy of 1.8 eV; in the latter case, starting particles are more stable, their bonds are stronger, and the final particle Si_{20} is low-stable, i.e., the binding energy is only 0.3 eV. It is clear that a strong

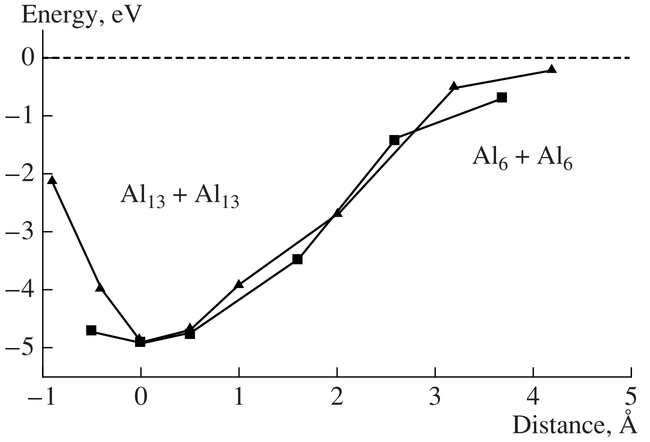

Fig. 7. Dependence of the interaction energy of aluminum nanoparticles on the distance between them.

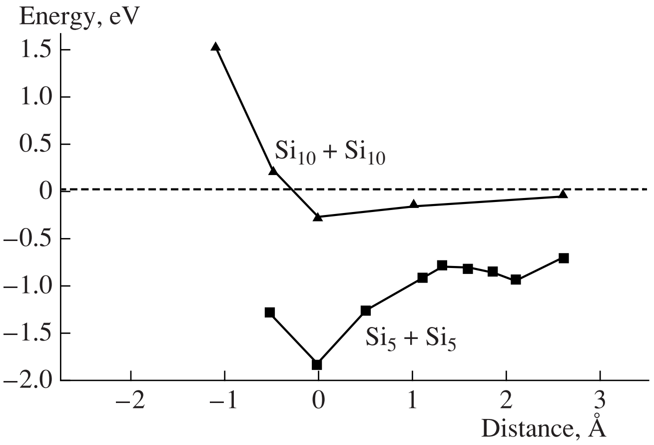

Fig. 8. Dependence of the interaction energy of silicon nanoparticles on the distance between them.

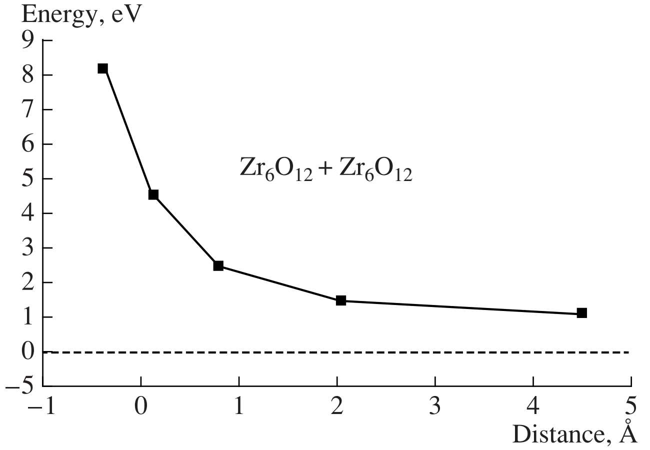

Fig. 9. Dependence of the interaction energy of zirconia nanoparticles on the distance between them.

bond of such particles requires thermal activation that promotes breaking of old bands and the formation of a new more stable atomic structure.

As expected, the behavior of zirconia nanoparticles is even more complex. Stable particles such as Zr_6O_{12} are repulsed from each other (Fig. 9). However, the consideration of unstable particles Zr_7O_{14} produced by splitting the stable particle $Zr_{14}O_{28}$ shows their strong barrierless attraction. Hence, mechanical activation and, certainly, a high temperature of the process can be very useful for reliable agglomeration of zirconia nanoparticles.

CONCLUSIONS

Thus, quantum-mechanical calculations show that nanoparticles with metal, covalent, and ionic bonds behave differently under mechanical deformation. The elastic modulus of aluminum (metal) particles nonlinearly depends on the strain; for silicon particles (with covalent bonds), the dependence of the elastic modulus on the strain is linear; for zirconia nanoparticles (with ionic bond), the elastic modulus is constant. In general, we can say that elastic characteristics of nanoparticles significantly (several times) exceed the corresponding values characteristic of bulk materials.

Approach of aluminum nanoparticles leads to their spontaneous strong adhesion; good adhesion between silicon nanoparticles requires thermal activation; zirconia nanoparticle agglomeration requires mechanical activation (rapid grinding and pressing).

ACKNOWLEDGMENTS

The author is grateful to A.A. Gnidenko, A.N. Chibisov, and M.A. Kulik for their participation in calculations.

This study was supported by the Presidium of the Far Eastern Branch of the Russian Academy of Sciences with computer support of the Computer Center of the Far Eastern Branch.

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