Influence of particle size distribution on nanopowder cold compaction processes

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Abstract. Nanopowder uniform and uniaxial cold compaction processes are simulated by 2D granular dynamics method. The interaction of particles in addition to wide-known contact laws involves the dispersion forces of attraction and possibility of interparticle solid bridges formation, which have a large importance for nanopowders. Different model systems are investigated: monosized systems with particle diameter of 10, 20 and 30 nm; bidisperse systems with different content of small (diameter is 10 nm) and large (30 nm) particles; polydisperse systems corresponding to the log-normal size distribution law with different width. Non-monotone dependence of compact density on powder content is revealed in bidisperse systems. The deviations of compact density in polydisperse systems from the density of corresponding monosized system are found to be minor, less than 1 per cent.

1. Introduction
Processes of cold compaction of nanosized powders are the grave problem for manufacturing the nanostructured ceramics by powder metallurgy methods. Large forces of interparticle adhesion, which result from intermolecular dispersion forces of attraction, and high strength of nanoparticles require to use very high pressures (of gigapascal range) to achieve densities desired at the compaction stage [1-6]. Theoretical search of most effective conditions of compaction processes takes here on special significance and topicality. However it is hampered by absence of a valid phenomenological theory describing the powder body properties. Thereupon the direct simulations of nanopowders by the granular dynamics method, also known as the discrete element method [4, 5, 7-11], have attractive prospects. Different regularities of nanopowder systems, for example, the size effect in nanopowder compaction processes, have been already investigated in the framework of the granular dynamics method [4, 5, 12, 13]. Heretofore objects for numerical experiments are monodisperse systems [8, 12, 13], which consist of particles of the same size, or systems with very artificial particle size distributions, for example, the uniform distribution into the given narrow range of sizes [9]. This situation differs drastically from real experimental conditions [1-3, 6].

It is unlikely that the influence of particle size distribution on the powder compressibility could be detected by full-scale experiments since here there are too many factors, which have an influence at one time. However some data [6] are rather evidence of presence such influence. Attempts of studying this problem in the frames of numerical experiments have been made earlier, for example, in Refs. [7, 11], where powders of micron sizes have been simulated. Interparticle interactions in such powders
have essential distinctions from the nanoparticle interactions, namely dispersion attraction of particles is negligible, the plastic deformation of particles play an important role, and so on.

2. Objects of study and investigation method
The aim of the present study is to analyze the influence of particle size distribution on the compressibility of nanopowder systems. To achieve the aim the processes of the uniform (two-sided) and the uniaxial (one-sided) compaction have been simulated by granular dynamics method in 2D geometry. The following systems are simulated: equigranular (monodisperse) systems with particle diameter \( d = 10, 20 \) and \( 30 \) nm; bidisperse systems with different content of small (the diameter is \( d_1 = 10 \) nm) and large (the diameter is \( d_2 = 30 \) nm) particles; polydisperse systems, which are described by the lognormal size distribution law with maximum at the diameter \( d_{\text{mp}} = 20 \) nm and different widths.

The particle size distribution for polydisperse systems is determined in the form of truncated lognormal law

\[
f_n(x) = \frac{f(x)}{I_n}, \quad f(x) = \frac{1}{x} \exp \left[ -\frac{(\mu - \ln x)^2}{2\sigma^2} \right], \quad \mu = \sigma^2 + \ln(d_{\text{mp}}),
\]

\[
I_n = \int_{d_{\text{min}}}^{d_{\text{max}}} f(x) \, dx, \quad d_{\text{min}} = d_{\text{mp}} \exp(\pm \sigma \sqrt{2\ln 6}),
\]

where \( I_n \) is the normalization integral, \( d_{\text{mp}} = 20 \) nm, and the limits \( d_{\text{min}} \) and \( d_{\text{max}} \) are determined by the condition of the function \( f(x) \) reduction by 6 times with respect to the maximum at \( x = d_{\text{mp}} \). Beyond the bounds of \( (d_{\text{min}}, d_{\text{max}}) \) the normalized function \( f_n(x) \) is fixed to zero. The systems with different distribution width are studied: \( \sigma = 0 \) (monodisperse system), 0.15, 0.30 and 0.47. The

![Figure 1. Examples of initial powder structures: (a) a bidisperse system with the relative fraction of small particles \( \omega = 0.8 \) (\( d_{\text{rep}} = 20 \)nm); (b) a polydisperse system, where the particle size distribution is described by the function of (1) with parameters \( \sigma = 0.47 \) and \( d_{\text{mp}} = 20 \) nm. Dashed lines show the model cell boundaries.](image-url)
maximal value $\sigma = 0.47$ corresponds to the real nanosized powders [5], which are produced by the method of electric explosion of wires [18].

The total number of particles $N_p$ in model cells has been set equal to 1000. At that, as test calculations show, a model cell is a reliable representative volume of the powder body, i.e., the influence of the cell sizes on the model system properties is negligible. The initial density of all model systems has been set equal to $\rho_0 = 0.5$. As the density we have used the relative area of the model cell, which is occupied by the particles, i.e., $\rho = S_p / S_{cell}$. To generate initial structures the algorithm of Ref. [12] is used, which allows producing isotropic and homogeneous structures in the form of connected 2D-periodical cluster. Figure 1 shows examples of initial structures. It is worth mention that the model polydisperse system with distribution width $\sigma = 0.47$ (see the figure 1-b) looks like real nanopowder photographs obtained by the scanning electron microscopy (see, for example, the figure 1 in Ref. [5]).

The parameters of interparticle interactions correspond to oxide nanosized powders having weak (I type systems) or strong (II type systems) agglomeration tendency [12, 13]. The theoretical model of [12, 13] includes the contact interaction laws, such as the modified Hertz law, which describes the elastic repulsion of particles, the linearized Cattaneo–Mindlin law [14, 15], which describes the “friction” forces at particle shift, the Lurie law [16], which describes the contact elasticity to the particle rolling, as well as modified Hamaker’s formula [17], which describes the dispersion attractive forces, and (in the case of II type systems) the possibility of interparticle solid bridges formation [10]. Note that the dispersion attractions and the agglomeration tendency for the nanosized powders, as distinct from powders of micron (or larger) sizes, take on special significance and, in particular, owing to introduction this factors the size effect in compaction processes, well-known from the experimental studies [1-3, 6], is reproduced by the granular dynamics method. All parameters of particle interactions have been described in [12, 13] in detail. An exception is only the utilization in the present 2D simulations, in contrast to 3D calculations of [12, 13], the larger value of the interparticle friction coefficient $\mu = 0.5$.

\[
\begin{align*}
\rho_0, \text{ MPa} & \quad 100 \quad 10 \quad 1 \quad 0.1 \quad 0.01 \quad 0.001 \quad 0.0001 \\
\rho & \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \quad 1
\end{align*}
\]

Figure 2. Compaction curves on the “density – pressure” plane: (a) process of uniform compaction of mono- and bidisperse systems of I type with different content of small particles: $\omega = 1.0$ (solid line), 0.9 (dashed line), 0.5 (dotted line), 0.0 (dashed-dotted line); (b) process of uniaxial compaction of the monosystem with the particle diameter $d = 20$ nm (solid line) and polydisperse systems of II type, which are described by the lognormal distribution law (1) with parameters $d_{up} = 20$ and $\sigma = 0.15$ (dashed line), 0.30 (dotted line), 0.47 (dashed-dotted line).
3. Results and Discussion

Figures 2 – 4 demonstrate the simulation results for bidisperse and polydisperse systems. Figure 2 shows the compaction curves, the curves each constructing on the basis of averaging 20 – 40 independent numerical experiments. The statistical accuracy is shown in figures 3 and 4, where compact densities corresponding to the fixed pressures are presented. As the relative fraction of small particles in the figure 3 we imply the quantity \( \omega = N_i / N_p \). The stress tensor \( \sigma_{ij} \), averaged over the model cell, is calculated by the known expression [8-10]:

\[
\sigma_{ij} = \frac{-1}{V_{cell}} \sum_{k<l} f_{ij}^{kl} r_{ij}^{kl},
\]

where the summation is conducted over all pairs \((k, l)\) of interacting particles, \( V_{cell} = S_{cell} d_{sv} \) and \( d_{sv} \) is the averaging particle diameter. Note that as the compaction pressure in the figures 2 – 4 we have used the main pressure \( p = -Sp(\sigma_{yy}) / 2 \) for the uniform compaction process and the axial pressure \( p_y = -\sigma_{yy} \) (along the loading \( y \)-axis) for the uniaxial compaction process.

Figure 2-a shows that for the bidisperse systems at the range of relatively small pressures (1 – 100 MPa) the compact density increases monotonically when passing from a system of small particles (with diameter \( d_1 = 10 \) nm) to a system of large particles (with diameter \( d_2 = 30 \) nm). At larger pressures, as the figure 3 shows, dependences \( \rho(\omega) \) of bidisperse systems become non-monotone: there is the maximum at the range of \( \omega \) values about 80 – 90 per cent. In the vicinity of the maximum the density values of bidisperse systems can exceed the densities of corresponding monosized systems by 1-2 per cent. In the systems of II type (see the figure 3-b) this phenomenon is expressed weaker but is on hand too.

The relative simple considerations can explain rather a sharp increase of the compact density when small number of large particles is added to the initial system of small particles, i.e., in the vicinity of \( \omega = 1 \). Into the area being occupied by the large particles added the density of the initial monodisperse system of small particles (\( \rho_1 < 1 \)) has been increased up to the maximal value equal to 1. At the condition that a large particle added does not effect on the density \( \rho_1 \) of surrounding monodisperse

![Figure 3](image-url)

**Figure 3.** Dependences of the density of bidisperse systems of I type (a) (the uniform compaction) and of II type (b) (the uniaxial compaction) on the relative fraction \( \omega \) of small particles. Solid lines (from the bottom) correspond to the compaction pressures \( p = 100, 200, 300 \) and 400 MPa; dashed-dotted lines show the compact densities after unloading from the maximal pressure (400 MPa); dashed lines are the asymptotes by Eq. (5).
system and also if \( d_1 \ll d_2 \) and \( S_2 \ll S_{\text{cell}} \), where \( S_2 \) is the area occupied by the large particles added, it is not difficult to deduce the density change. The density of the initial monodisperse system of small particles and the new density of the bidisperse system are determined by the expressions

\[
\rho_i = \frac{N_p (\pi / 4) d_i^2}{S_{\text{cell}}}, \quad \rho = \frac{N_1 (\pi / 4) d_1^2 + N_2 (\pi / 4) d_2^2}{S_{\text{cell}}},
\]

where \( N_1 = \omega N \), \( N_2 = (1-\omega)N \). The new number of particles \( N = N_1 + N_2 \), which are situated into the area of the initial model cell, is \( N = N_p + N_2 - \Delta N_1 \). The number \( \Delta N_1 \) of “displaced” small particles, which was situated into the area \( S_2 = N_2 (\pi / 4) d_2^2 \), is \( \Delta N_1 = S_2 \rho_i \left[ (\pi / 4) d_2^2 \right] \). Combining above listed expression and Eq. (3) we get

\[
\Delta \rho = \rho - \rho_i = \rho_i (1-\rho_i) \frac{d_2^2}{d_1^2} \frac{(1-\omega)}{1 + (1-\omega) \left[ \rho_i (d_2 / d_1)^2 - 1 \right]}. \tag{4}
\]

In the limit of \( \omega \to 1 \) this expression gives the asymptotic dependence of the bidisperse system density on the content \( (\omega) \) in the form of

\[
\rho(\omega) = \rho_i + (1-\omega) \rho_i (1-\rho_i) \frac{d_2^2}{d_1^2}. \tag{5}
\]

The asymptotic dependences of (5) are shown by dashed lines in the figure 3. Noticeable deviations of simulation curves \( \rho(\omega) \) from the asymptotes (5) in the limit \( \omega \to 1 \) are connected with weak implementation of the condition \( d_1 \ll d_2 \) in the bidisperse systems being studied, where we have \( d_2 / d_1 = 3 \).

Figure 4 shows the compaction processes simulation results for polydisperse systems. The uniaxial compaction curves of II type systems, which are demonstrated in the figure 2-b, reveals that visible distinctions of compressibility of the systems simulated are only observed at the range of relatively

![Figure 4](image-url)

**Figure 4.** Dependences of the densities of polydisperse systems of I type (a) (the uniform compaction) and of II type (b) (the uniaxial compaction) on the parameter \( \sigma \), which determines the width of size distribution (1). Solid lines (from the bottom) correspond to the compaction pressures \( p = 100, 200, 300 \) and 400 MPa; dashed-dotted lines show the compact densities after unloading from the maximal pressure (400 MPa).
small pressures \( p_c \), namely for pressure values \( p_c < 10 \) MPa. At larger pressures the density differences become insignificant. Figure 4 demonstrates the density dependences at fixed compaction pressure on the particle size distribution width, which is determined by the parameter \( \sigma \) in Eq. (1). It can be seen that in the range of \( \sigma < 0.1 \), i.e., in the vicinity of pure monosized system the minor deterioration of compressibility is observed. It is possible that this deterioration is caused by the destruction of quasi-crystallinity regions, which are intrinsic for monodisperse systems [8]. Further increase of parameter \( \sigma \) results in compressibility improvement, i.e., the compact densities begin to go up. However as a whole, as the figure 4 shows, in the range of high compaction pressures ( \( p_c > 10 \) MPa) the transition from a monodisperse system to polydisperse systems have an insignificant influence on the density of the nanosized powder. Density changes do not exceed 1 per cent. This result justifies the application of monodisperse systems in the frameworks of granular dynamics method to describe the experimental properties of real polydisperse nanopowders. It is worth mention here that the rigorous foundation for the last statement requires the fulfillment of numerical experiments in 3D geometry. This remark concerns also the results obtained for bidisperse systems. In particular, the asymptotical dependence (5) in 3D geometry has a form of

\[
\rho(\omega) = \rho_1 + (1-\omega)\rho_1(1-\rho_1) \frac{d_1^2}{d_2^2}.
\]

It can result in much larger maximums at the dependences \( \rho(\omega) \) demonstrated in the figure 3.

4. Conclusion

Compaction processes of mono-, bi- and poly-disperse nanopowder systems are simulated by the granular dynamics method in 2D geometry. The main results of the research are as follows:

1. The influence of the content of bidisperse systems (composed of particles with diameter \( d_1 = 10 \) nm and \( d_2 = 30 \) nm) on the powder compressibility has been studied. The non-monotone density dependence on the relative fraction of small particles \( \omega = N_1 / (N_1 + N_2) \) has been revealed; namely, the dependence \( \rho(\omega) \) has a maximum in the vicinity of values \( \omega = 0.8 - 0.9 \), where the bidisperse system density can exceed by 1-2 per cent the densities of corresponding monodisperse systems.

2. The compressibility of polydisperse systems with lognormal particle size distribution law has been studied. It is revealed that the increase of the distribution width, which is determined by the parameter \( \sigma \), from zero (a monodisperse system) up to the value \( \sigma = 0.47 \) that corresponds to real nanopowders, has an insignificant influence on the compact density. This result justifies the application of monodisperse systems in the frameworks of granular dynamics method to describe the experimental properties of real polydisperse nanopowders.

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