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Compressibility of the structural and functional ceramic nanopowders

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Abstract

The work aim was the quantitative comparison of compressibility parameters of different dry nanostructured ceramic powders using coefficients of the compaction equation in dimensionless form. Pressing characteristics of different nanopowders manufactured by diverse methods were investigated: ZrO_2–Y_2O_3; Al_2O_3–MgO; Al_2O_3; (Ba,W)TiO_3; (Ba,Sr,Ca)TiO_3; Pb(Zr,Ti)O_3. Dry compaction was carried out by the common uniaxial pressing and under powerful ultrasound action (PUA). It was shown that the dimensionless compaction equation describes the compaction diagrams of dry ceramic nanopowders with high reliability and its coefficients allow to characterize quantitatively the compressibility of different powders. The production methods of nanopowders even the same chemical composition determine the pressing characteristics of dry cold compaction. YSZ nanopowders manufactured by plasma-chemical or chemical synthesis have essentially different compressibility parameters. PU-action during dry pressing shows the most efficiency for ceramic nanopowders having metastable structure and not uniform morphology.

Keywords: Pressing; Al_2O_3; $BaTiO_3$ and titanates; PZT; Spinels; ZrO_2

1. Introduction

The previous investigations have shown efficiency of a dry uniaxial pressing nanostructured powders under powerful ultrasound action (PUA) for manufacturing structural and functional nanoceramics.[1–3] At optimum conditions of nanopowder compaction the method ensures uniform density distribution in articles having a complex form owing to even packaging particles when their vibration displacement is comparable with a particle or agglomerate size. Also interparticle and die-wall friction forces decrease under PUA which promotes fracture of agglomerates and nanostructure formation at sintering green compacts due to effects of mechanoactivation of particles.[4] The method eliminates application of plasticizers and binders as potential sources of impurities.

However to optimize the manufacturing methods of different functional and structural ceramics it is necessary to have comparative and comparable quantitative densification characteristics of powders with different compositions. As such characteristics it is possible to use coefficients of a logarithmic compaction equation in the dimensionless form:[1]

$$\rho = b \ln \left(\frac{P_{pr}}{P_{cr}} \right) + 1 \quad (1)$$

where ρ is the relative density of a green compact, P_{pr} the compaction pressure and b is the constant describing densification intensity (compressibility) of compacted powder at any P_{pr} value:

$$\frac{d\rho}{dP_{pr}} = \frac{b}{P_{pr}} \quad (2)$$

P_{cr} is the extrapolated value of the critical compaction pressure at which the void-free condition of a green compact is reached:

$$\rho(P_{cr}) = 1 \quad (3)$$

P_{cr} value defines a yield point of the powder body under press and so characterizes the powder body plastic properties.

Coefficients b and P_{cr} fully characterise a behaviour of a powder body during its strain. The increase b specifies the increase of densification intensity; the decrease P_{cr} points to improvement of plastic properties of a powder body.

The work aim was the quantitative comparison of compressibility parameters of different dry nanostructured ceramic powders using coefficients of the compaction equation in dimensionless form.

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2. Experimental procedures

Dry pressing characteristics of the nanostructured powders of different ceramic compositions and manufactured by diverse methods were investigated:

(1) ZrO_2–5 wt.% Y_2O_3 (TZ-3YS-E, TOSOH, Japan); specific surface area of $S_{BET} = 6.4 \pm 0.5\ m^2/g$.
(2) Spinel Al_2O_3–MgO (S30CR, Baikalox, USA); $S_{BET} = 30 \pm 5\ m^2/g$.
(3) $(Ba_{0.6}Sr_{0.3}Ca_{0.1})TiO_3$ (BSCT, Korea Electronics Co., Korea); average particle size of 50 nm.
(4) $BaTi_4O_9 + BaWO_4$ (BWTO, CIJ Co., Korea); $S_{BET} = 5 \pm 1\ m^2/g$.
(5) Al_2O_3 (Siberian Chemical Industrial Complex (SCIC), Russia); $S_{BET} = 10 \pm 1\ m^2/g$.
(6) ZrO_2–5 wt.% Y_2O_3 (PZY-8, SCIC, Russia); $S_{BET} = 7 \pm 1\ m^2/g$.
(7) $Pb(Zr_{0.54}Ti_{0.46})O_3$ (PZTSt-5, SCIC, Russia); average particle size of 100 nm.

Examined powders had different morphology of particles depending on the manufacture methods: TZ-3YS-E, S30CR were made by the production technologies of chemical synthesis (CS); BSCT and BWTO by sol–gel method with consequent spray-drying (SD); PZY-8, Al_2O_3, PZTSt-5 by the plasma-chemical synthesis (PC) with the resulting formation of particles having metastable structure and not uniform morphology (spheres, polycrystalline scales).

Cold uniaxial compaction of powders was carried out in the steel cylindrical moulds being acoustic waveguides. The inner diameter was 10, 14 and 50 mm, the compaction pressure was selected over the range $P_{pr} = 80$–800 MPa. During pressing the PUA was applied to a mould at different power of the ultrasonic generator over the range $W_{PUA} = 0$–3 kW by the technique described in.[1–3] Compaction diagrams of each material in different pressing conditions were obtained under developed procedure of consecutive loading-unloading using on-line computer analysis of the powder densification (via a punch displacement) versus change of compaction pressure.[5] The compaction diagrams were constructed on five and more points; each point grew out averaging not less than three experiments. Approximation of experimental data was performed by the least-squares method. For each powdered material the experimental constant coefficients b and P_{cr} of the compaction equation and approximating reliability R^2 have been defined.

3. Results and discussion

Results of experimental data interpretation are presented in Table 1.

Table 1
Compressibility parameters of different nanopowders

Powder type, chemical composition	Production method	S_{BET} (m^2/g) (d_p, nm)	W_{PUA} (kW)	P_{cr} (MPa)	b	R^2 (%)
PZTSt-5 PC, PZT ($Pb(Zr_{0.54}Ti_{0.46})O_3$)	PC	(100)	0	1.87×10^4	0.1039	99.9
			1	1.33×10^4	0.1140	99.7
PCY-8 YSZ (ZrO_2–5 wt.% Y_2O_3)	PC	7 ± 1	0	8.26×10^4	0.0939	99.8
			1	8.74×10^4	0.0932	99.9
			2	1.20×10^5	0.0888	99.6
			3	1.67×10^5	0.0861	100.0
TZ-3YS-E YSZ (ZrO_2–5 wt.% Y_2O_3)	CS	6.4 ± 0.5	0	1.22×10^8	0.0390	98.9
			1	1.38×10^8	0.0387	99.4
			2	1.82×10^8	0.0379	99.1
			3	5.23×10^8	0.0354	98.4
Al_2O_3	PC	10 ± 1	0	1.13×10^5	0.1009	99.8
			1	1.11×10^5	0.1018	99.7
			2	9.65×10^4	0.1028	99.9
			3	1.13×10^5	0.1020	99.4
S30CR spinel (Al_2O_3–MgO)	CS	30 ± 5	0	1.54×10^7	0.0514	98.6
			1	1.46×10^7	0.0519	99.6
			2	1.73×10^7	0.0512	99.7
			3	1.83×10^7	0.0511	99.1
BWTO $BaTi_4O_9 + BaWO_4$	SD	5 ± 1	0	1.06×10^5	0.0637	99.1
			1	1.15×10^5	0.0617	99.5
			2	1.58×10^5	0.0583	99.9
			3	5.40×10^4	0.0719	99.8
BSCT $(Ba_{0.6}Sr_{0.3}Ca_{0.1})TiO_3$	SD	(50)	0	1.49×10^6	0.0510	99.4
			1	1.50×10^6	0.0509	99.9
			2	1.21×10^6	0.0523	99.8
			3	1.64×10^6	0.0503	99.5
Cu	WEE	(<500)	0	1.93×10^3	0.1422	99.5
			2	1.82×10^3	0.1431	99.7

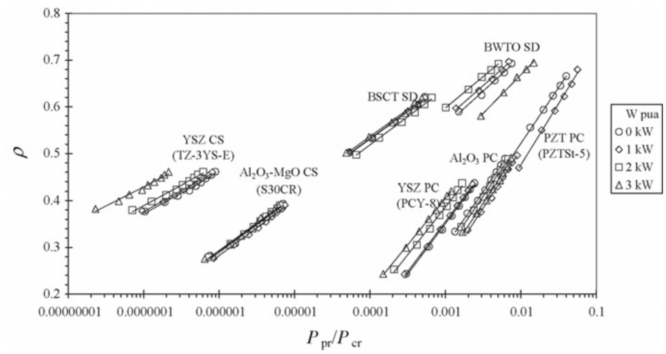

Fig. 1. The compaction diagrams of different ceramic nanopowders for common dry uniaxial pressing and under powerful ultrasound action (experimental data).

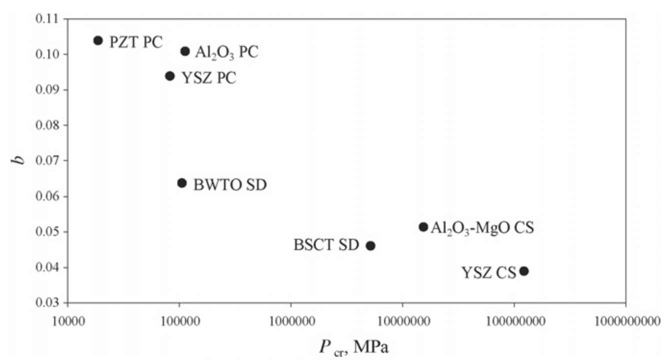

Fig. 2. The compressibility parameters of different ceramic nanopowders for common dry uniaxial pressing.

Received data specify that compressibility characteristics essentially differ for various types of powders (Figs. 1–5). Fig. 1 shows experimental data. Figs. 2–5 reflect calculations carried out by the Eq. (1) using least-squares procedure.

Irrespective of a material chemical composition the powders produced by the plasma-chemical synthesis show most intensive densification (have the greatest value of the coefficient $b \approx 0.1$). These powders have rather low value of the critical compaction pressure $P_{cr} \approx (10^4–10^5)$ MPa.

A little bit smaller compressibility intensity $b \approx 0.05–0.07$ have the powders manufactured using the spray-drying method. However, the critical compaction pressure values for these powders change in the wider range $P_{cr} \approx (10^4–10^6)$ MPa.

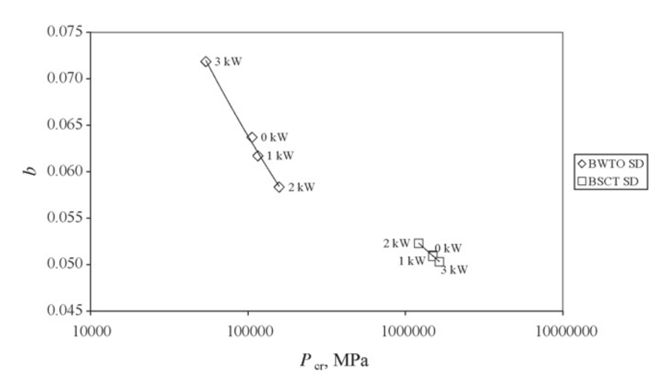

Fig. 3. The change of the compressibility parameters under powerful ultrasound action for BWTO, BSCT powders produced using spray-drying method.

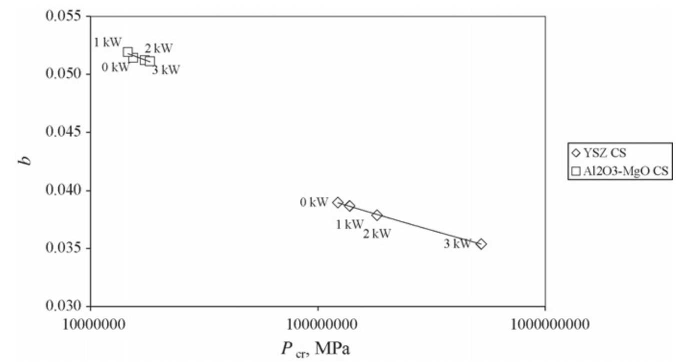

Fig. 4. The change of the compressibility parameters under powerful ultrasound action for YSZ and spinel powders produced by the chemical synthesis.

The worst dry compressibility characteristics reveal the powders produced by the chemical synthesis technology. Intensity of their densification at dry cold pressing in the shut hard dies is enough low ($b \approx 0.03–0.05$), and the critical compaction pressure is high $P_{cr} \approx (10^7–10^8)$ MPa.

The compressibility characteristics for yttrium-stabilized zirconia (YSZ) powders produced by the diverse methods (PC or CS) essentially differ: the P_{cr} of YSZ PC powder (PZY-8) is four orders of magnitude greater and compressibility intensity b is two to three times smaller than for YSZ CS (TZ-3YS-E).

Among investigated powders the greatest compressibility intensity and the lowest value of critical pressure have the PZTSt-5 powder also manufactured by the plasma-chemical synthesis.

$Ba_{0.6}Sr_{0.3}Ca_{0.1}TiO_3$ powder has adverse dry pressing characteristics (low b and high P_{cr} parameters).

Dependencies of the compressibility characteristics versus PUA power are not so significant for some kinds of powders (Figs. 3–5). However, revealed changes of b and P_{cr} parameters for dry compaction at PU-action specify following features.

For four of seven investigated ceramic nanopowders (PZTSt-5, Al_2O_3, BWTO, BSCT) there is the optimal magnitude of PUA power at which the P_{cr} parameter takes the minimum value, but the b coefficient has a maximum. These features can be explained by the known effects of ultrasound impact on solid state. Decrease of the critical compaction pressure is caused by the lowering strength of interparticle

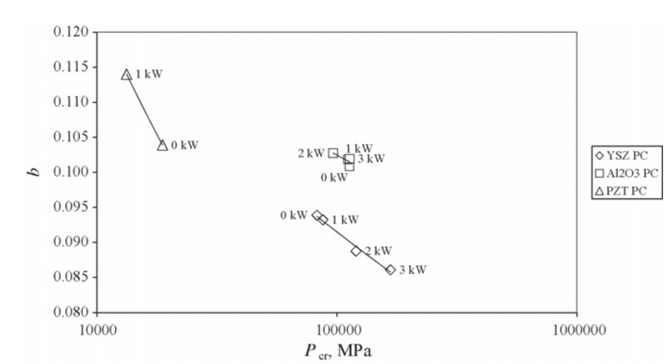

Fig. 5. The change of the compressibility parameters under powerful ultrasound action for YSZ, alumina and PZT powders produced by the plasma-chemical synthesis.

links in nanopowder agglomerates under action of powerful ultrasonic vibration; increase of the compressibility intensity results from reduction of the interparticle and die-wall friction forces.[3,4]

The compressibility intensity of S30CR (Al_2O_3–MgO), Al_2O_3 and BSCT powders have little or no effect from PU-action during compaction. However, for alumina and BSCT nanopowders a 14–18% reduction in critical pressure was achieved at optimum level of ultrasonic power W_{PUA} (1 and 2 kW, correspondingly).

Increasing W_{PUA} at compaction TZ-3YS-E and S30CR results in increase of P_{cr} value and little diminution of the b coefficient.

The compaction diagram parameters for copper nanopowder manufactured by the method of wire electrical explosion (WEE) in the R&D Institute of High Voltage at Tomsk Polytechnic University are presented in the table for comparison. These diagrams practically coincide for common uniaxial static pressing and compaction under PU-action owing to plasticity of a copper powder. But the ultrasound influences the value of critical pressure: P_{cr} in case of PU-action is less than at usual pressing by 6%.

Thus, the analysis of parameters of the compaction equation in the dimensionless form allows to consider the influence of pressing conditions as well as production methods of powders on efficiency of dry densification, to determine the optimum conditions of compaction under PU-action for manufacturing qualitative ceramic articles.

4. Conclusions

1. The logarithmic compaction equation in the dimensionless form describes the compaction diagrams of dry ceramic nanopowders with high reliability (no less than 98%) and its coefficients allow to characterize quantitatively the compressibility of different powders at dry pressing in the shut dies.
2. The production methods of nanopowders even the same chemical composition determine the pressing characteristics of dry cold compaction. YSZ nanopowders manufactured by different methods (plasma-chemical synthesis or chemical synthesis) have essentially different compressibility parameters; their critical compaction pressure varies within four orders and compressibility intensity differs in two to three times.
3. Powerful ultrasound action during dry pressing shows the most efficiency for ceramic nanopowders having metastable structure and not uniform morphology (e.g. for powders manufactured by the plasma-chemical synthesis).

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References

1. Khasanov, O. L., Pokholkov, Yu. P., Sokolov, V. M., Dvilis, E. S., Bikbaeva, Z. G. *et al.*, Particularities of powerful ultrasound action on nanostructured powders. In *Proceedings of the Materials Research Society Symposium, vol. 520*, ed. G. Beaucage, J. E. Mark, G. T. Burns and D. M. Hua. Materials Research Society, Warrendale, PA, 1998, pp. 77–82.
2. Khasanov, O. L., Pokholkov, Yu. P., Ivanov, Yu. F., Ljubimova, L. L. and Makeev, A. A., Effect of ultrasonic compaction of nanopowder on structure and fracture character of zirconia nanoceramics. In *In Fracture Mechanics of Ceramics*, *vol. 13*, ed. R. C. Bradt, D. Munz, M. Sakai, V. Ya. Shevchenko and K. White. Kluwer Academic/Plenum Publishers, New York, 2002, pp. 503–512.
3. Khasanov, O. L., Dvilis, E. S., Sokolov, V. M. and Pokholkov, Yu. P., Ceramic powders dry compaction under powerful ultrasound action. *Key Eng. Mater.*, 2004, **264–268**, 73–76.
4. Khasanov, O. L., Karban, O. V. and Dvilis, E. S., Investigation of structural hierarchy of nanoceramics compacted by dry pressing under powerful ultrasound action. *Key Eng. Mater.*, 2004, **264–268**, 2327–2330.
5. Khasanov, O. L., Dvilis, E. S. and Sokolov, V. M., Plotting of compaction curves of ceramic powders on the basis of one-parameter pressing equation. *Refract. Indust. Ceram.*, 2001, **42**(1), 37–40.