Nanopowder net-shaping for manufacturing nanostructured ceramics

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ABSTRACT

This work is focused on the development of uniform compacting of dry nanopowders into complex shapes for sintering dense nanostructured ceramics and composites. New techniques of dry nanopowder compacting under ultrasonic action and collector compacting have been developed. The first one is based on the application of powerful ultrasonic vibration (PUV) to a special die (acoustic waveguide filled by nanopowder) simultaneously with uniaxial compaction pressure at room temperature. The collector technique involves specially designed molds, where active and passive shaping surfaces are combined in one shaping member of the mold according to the principle of minimizing die-wall friction forces and specific rules of collective motion of the shaping members.

Keywords: nanopowder, net-shaping, uniform compacting, nanopowder compacting, nanoceramics.

1 INTRODUCTION

In processing of bulk nanostructured ceramic/composite articles, it is important to compact a dust-like nanopowder into a required shape having uniform density without gradients of internal stresses and to prevent grain growth, warping, and other distortions during green body sintering [1]. These tasks are complicated by the increased friction at particle-particle and particle-die interfaces due to the larger specific area and higher surface reactivity of nanoparticles, facilitating their agglomeration and grain growth. It is also desirable to obtain uniform nanoscale structure and full density without adding any binders or plasticizers that can contaminate final product.

In search for solutions to these problems, two methods of dry nanopowder compaction have been developed and applied in processing of $(Ba,Sr,Ca)TiO_3$, $(Ba,W)TiO_3$, ZrO_2-5wt%Y_2O_3 functional and structural nanoceramics.

2 COMPACTION UNDER POWERFUL ULTRASOUND ACTION

The method of compaction under ultrasound action is based on the application of powerful ultrasonic vibration (PUV) to a special die (acoustic waveguide filled by nanopowder) simultaneously with uniaxial compaction pressure at room temperature [2, 3].

In many applications of the conventional uniaxial compaction, a liquid binder has to be added to the powder for reducing frictional force at the die wall by lubrication. However application of binders can lead to formation of additional porosity or impurities after burnout and sintering.

Alternatively, inter-particle and die-wall frictional forces can be effectively reduced by imposing mechanical vibrations on dry powders [4]. In the case of dry uniaxial compaction of nanopowders under PUV action, it is important to determine the optimal ultrasound power and amplitude at a certain resonance frequency for a given die (acoustic waveguide). In our setup, an ultrasonic generator with the frequency f of about 20 kHz and power W from 0.5 kW to 3 kW produced PUV amplitude from 0.5μm to 500μm.

By creating quasi-resonance conditions when the PUV amplitude is proportional or equal to multiples of the particle or agglomerate mean size, it is possible to uniformly pack nanoparticles during pressing.

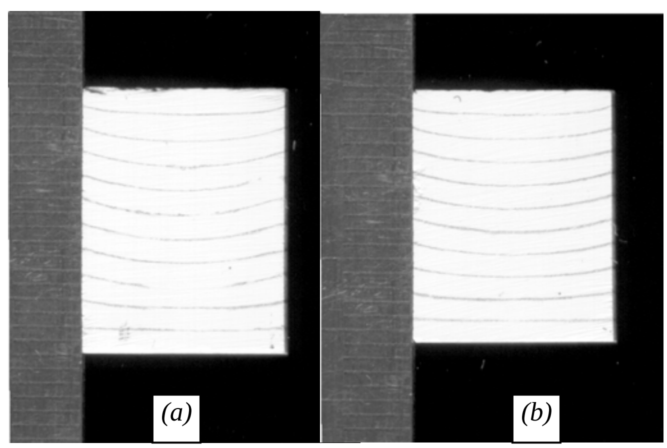


Figure 1: Density distribution in the $(Ba,W)TiO_3$ nanopowder green compacts after conventional compaction *(a)* and pressing under PUV *(b)*. Thin dark layers were formed by Cu nanopowder added as a marker. The scale is 1 mm.

A more uniform density distribution in the $(Ba,W)TiO_3$ nanopowder green compact was obtained after compaction under PUV (f = 22 kHz, W = 3 kW, compaction pressure P = 750 MPa) in comparison with the conventional uniaxial pressing at the same P (Fig.1). The relative density differential throughout the green compact height was

$\Delta\rho/\Delta h$ = 0.00156 for a sonicated compact having height H = 17.8 mm and relative density ρ = 0.7176. The conventional pressing yielded a sample with H = 18.8 mm, ρ = 0.6954, and $\Delta\rho/\Delta h$ = 0.00240, which was 35% above the value for the sonicated sample.

Figure 2 shows the influence of PUV action during compaction of (Ba,Sr,Ca)TiO_3 nanopowder with the mean particle size of 100 nm on the density of sintered ceramics.

This is a rigid powder with high elastic aftereffect (springback). Therefore, the dependence of green density (not shown in the figure) and fired density ρ vs compaction pressure P is non-monotonic: at higher P elastic interaction of nanoparticles results in the decrease of ρ. For every value of compaction pressure, there is an optimal level of ultrasound intensity leading to maximum density of sintered ceramics: W = 1 kW at $P \approx$ 150 MPa (curve Δ in Fig.2) and W = 3 kW at $P \approx$ 100 MPa (curve □).

In addition to better densification, ultrasonic compaction allows to improve the green compact strength. After conventional compaction with P < 150 MPa, thin discs of (Ba,Sr,Ca)TiO_3 nanopowder with height H = 1.2 mm and diameter D = 50 mm were not strong enough for handling. They got broken at ejection of green compact from the mold (curve ○). However such discs were successfully compacted without failure at P = 74 MPa under PUV action with W = 3 kW (curve □ in Fig. 2).

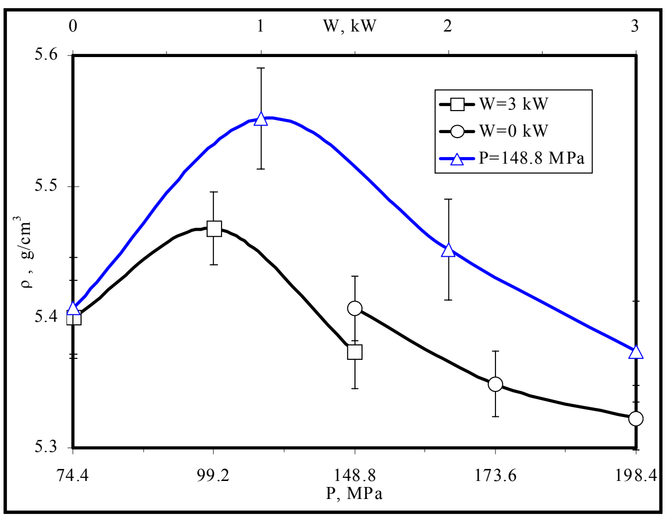


Figure 2: Density of sintered (Ba,Sr,Ca)TiO_3 ceramics vs nanopowder compaction pressure P for conventional compaction (○), ultrasonic compaction (□), and ρ vs W (top axis) at P = 148.8 MPa (Δ).

For better compaction, a higher PUV amplitude can be applied to the powder directly before pressing in the same mold in order to break agglomerates and activate nanoparticles.

Apparently, the application of PUV during compacting of nanopowders influences grain growth in the subsequent sintering and leads to formation of nanostructured ceramics. We obtained the grain size of 20 nm in ZrO_2-5wt%Y_2O_3 ceramics sintered after PUV compacting versus 500 nm grain size in the same ceramics compacted by the conventional technique [5]. A less dramatic but still very distinct decrease in the grain size was measured in (Ba,Sr,Ca)TiO_3 ceramics sintered after nanopowder compaction under PUV action (Fig. 3). The data also confirm that ultrasonic compaction of powder promotes more uniform distribution of grain size in sintered ceramics.

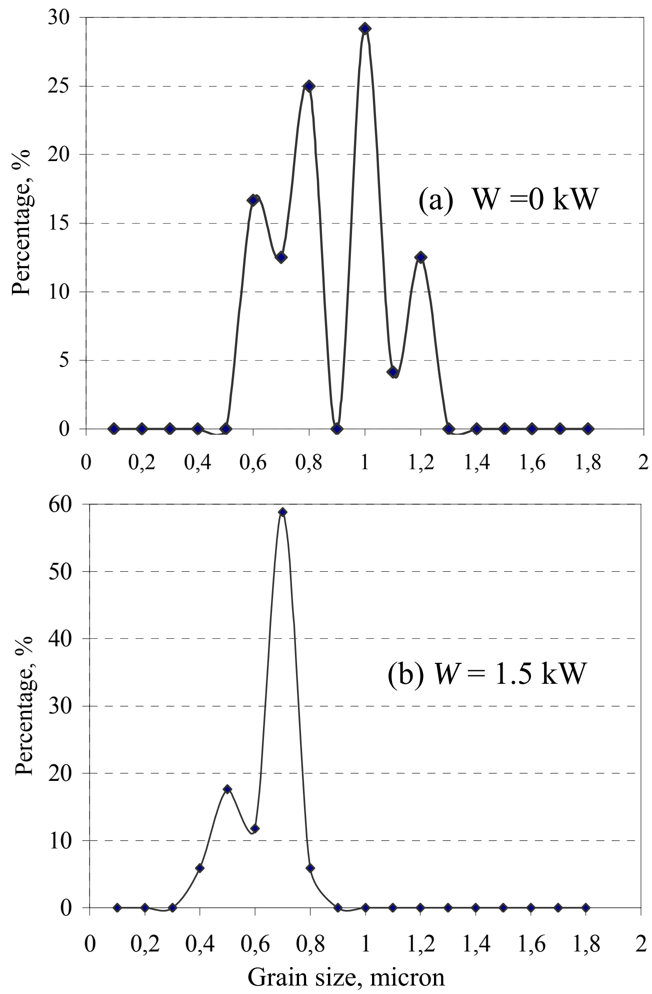
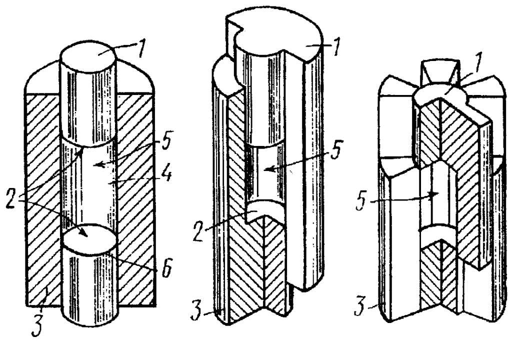


Figure 3: Granularity of (Ba,Sr,Ca)TiO_3 ceramics sintered at 1450°C (SEM data). Green compacts were pressed by conventional technique *(a)* and under PUV action at W = 1.5 kW (*b*).

3 COLLECTOR COMPACTION TECHNIQUE

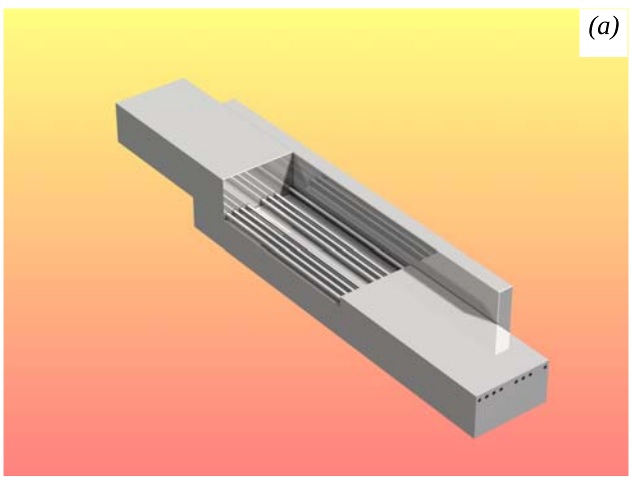
The collector technique involves specially designed molds (Figure 4), where active (2) and passive (5) shaping surfaces are joined in one shaping member (1, 3 in Fig.4 *b*, *c*) of the mold according to the principle of minimizing die-wall friction forces and specific rules of collective motion of the shaping members [6].



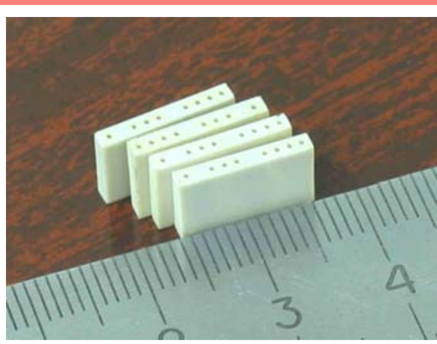
(a) (b) (c)

Figure 4: Mold designs for conventional uniaxial compaction *(a;* 1,6 - punches; 3 - die; 4 - shaping cavity*)* and for “collector” technique *(b), (c).*

This technique combined with ultrasonic action proved to be effective for shaping (Ba,W)TiO_3 nanopowder in manufacturing ceramic cases for microwave duplexers. The starting powder with mean particle size of 50 nm was compacted at uniaxial pressures from 100 MPa to 1.05 GPa by the conventional pressing and under PUV at *W* from 1.5 kW to 3 kW, and sintered at 1360^{o}C for 3 hours. The sintered cases consisted of grains with the mean size of 100-150 nm and had dimensional tolerance of ±5µm (Figure 5).



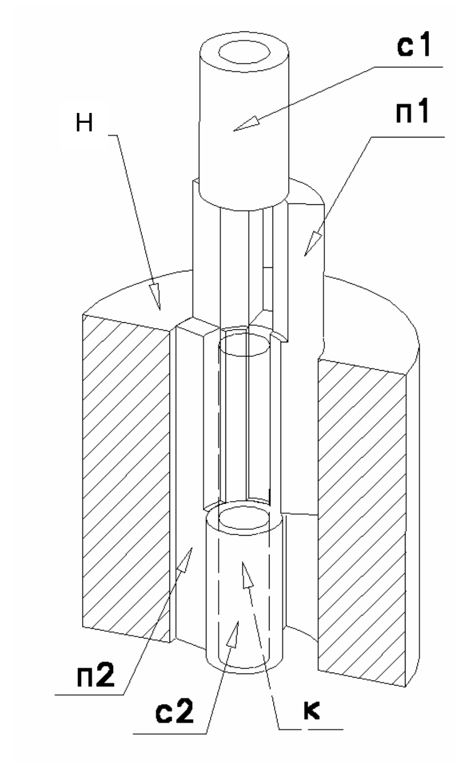
(a)



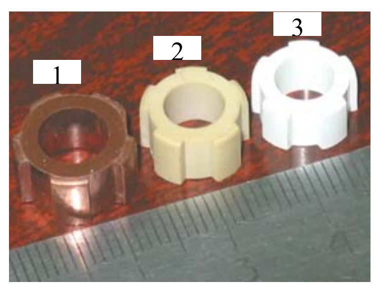
(b)

Figure 5: Cross-section of shaping members of collector mold *(a)* for compaction of ceramic cases of microwave duplexers from (Ba,W)TiO_3 nanopowder *(b).*

Another example of the collector technique application to shape nanopowders for manufacturing of impellers of gasoline pump is shown in Figure 6.



(a)



(b)

Figure 6: Cross-section of shaping members of collector mold *(a)* to compact impellers for gasoline pump *(b)* from Cu (1), (Ba,W)TiO_3 (2) or ZrO_2-5wt%Y_2O_3 (3) nanopowders.

n1 and n2 - shaping members joining active and passive shaping surfaces; c1 and c2 – punches to form front rings; k – insert to form hole (chain lines); **H** – holder.

CONCLUSION

Application of powerful ultrasonic vibration during dry pressing of different nanopowders ((Ba,Sr,Ca)TiO_3, (Ba,W)TiO_3, ZrO_2-5wt%Y_2O_3)) improves quality of both the green compacts and the sintered ceramics.

Optimization of ultrasound power and amplitude at a certain resonance frequency provides uniform packing of nanoparticles during pressing, better density and strength of green compact. When applied directly before pressing, PUV can break agglomerates and activate nanoparticles for subsequent sintering. This influences the grain growth during sintering and leads to formation of uniform nanostructure.

In combination with the collector compaction technique, PUV is effective for net-shaping of structural and functional ceramic articles with complex shape.

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