

Activation of consolidation processes of alumina ceramics

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Abstract. The methods for activating sintering ceramics based on Al_2O_3 by mechanical activation in the planetary mill, by adding in the mixture of nanopowders (NP) Al, Al_2O_3 , and submicron powder TiO_2 , and by applying the technology of spark plasma sintering (SPS) are developed. It has been shown that adding the nanopowder up to 20 wt. % Al_2O_3 in a coarse powder $\alpha\text{-Al}_2\text{O}_3$ activates the sintering process resulting in increased density and hardness of the sintered alumina ceramics. Substantial effect of increasing density of alumina ceramics due to adding the submicron powder TiO_2 in the compound of initial powder mixtures has been established.

1. Introduction

Compacting ceramic powders can be carried out using cold pressing with static one- or two-sided application pressure; hot pressing; cold or hot isostatic pressing in hydro- or gazostats; hot extrusion; slip casting; magnetic pulse, impact molding and explosive compacting; ultrasonic compaction. Nevertheless, the complexity and poor performance technology of hot and hot isostatic pressing [1-2] allowing to obtain materials with high strength properties [3] prevent the wide practical use of solid alumina ceramics. A relatively simple technique of uniaxial pressing with following sintering generally cannot produce ceramics with the high level of mechanical properties [4]. Therefore the problem of activating processes of consolidation alumina ceramics is of practical importance.

The aim of this work is to develop methods to activate the sintering process of the ceramics based on Al_2O_3 powders by mechanical treatment in a planetary ball mill and adding to the mixture of nanopowders (NP) Al, Al_2O_3 and submicron powder TiO_2 as well as application of spark plasma sintering (SPS) technology.

2. Experiment

Industrial nanocrystalline oxide powders (NP) Al_2O_3 , $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$ of the ultra-dispersed type obtained by a plasma-chemical synthesis (PCS) were used. Chemical composition of the powders is given in table 1.

Table 1. Chemical composition of initial plasma-chemical oxide powders (mol %).

Number	Al_2O_3	ZrO_2	Y_2O_3
1	100	-	-
2	80	19	1

Besides plasmachemical nanopowders, the coarse-grained powder Al_2O_3 – pure alumina, technical grade alumina and white electrocorundum (see table 2) were used in the work. White electrocorundum



is widely used in the alumina ceramics technology. Its sintering temperature is not less than 1800°C [5]. To reduce the temperature the submicron powder TiO_2 with a particle size of 0.5...2 μm in the amount of 1.5 wt.% was added to the white alumina powder.

Table 2. Chemical composition of white electrocorundum.

Type	Mass fraction (%), no more			
	Al_2O_3	SiO_2	Na_2O	Fe_2O_3
25A	99.1	0.1	0.26	0.06

Electroexplosive NP Al was used as an activating additive. Average surface diameter of particles of the NP ($d_{\text{av}}=60000/\rho S_{\text{sp}}$, where ρ – density, g/cm^3 , S_{sp} – specific surface of the powder, cm^2/g) determined with a help of gas adsorption (method BET) was not exceed 140 nm.

Sieve analysis of the coarse powders pure alumina and technical alumina was carried out using the analyzer A 20. Powder samples of 50 g weight were used for analysis. The frequency of a vibrator was 70 Hz, the sieving time – 10 minutes. After sifting fractions were weighed and content of each was calculated. The bulk and tap density, flowability of investigated powders were determined.

Oxide powders were annealed in air atmosphere in a high temperature resistance furnace at 1450°C for one hour for phase transition from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$.

To improve processing characteristics and enhancing the activity of annealed powders they were mechanically activated in the planetary ball mill Activator 2SL for 20 minutes at a rotation speed of the grinding vessels of 30 Hz. Zirconia balls were as grinding bodies. As a result of the mechanical action there is a significant plastic deformation at the vicinity of interparticle contacts. In order to define an activating effect of the mechanical treatment on the consolidating process the white electrocorundum was processed at different modes (rotation frequency of the grinding vessels f – 20 and 30 Hz, the time of treatment τ – 10, 20, 30 and 40 minutes for each frequency).

After the treatment the powder mixtures were sieved through a sieve 0045 for 10 minutes using vibratory drive C.1 to obtain the fraction $< 45 \mu\text{m}$ and plasticized with an aqueous solution of carboxymethyl cellulose (CMC) at the rate of 5 wt. % CMC and 95% a powder. After granulation and drying the plasticized powders were molded using uniaxial pressing in a steel mold. The obtained compacts were cylinders of diameter $10 \pm 0.01 \text{ mm}$ and a height of $5 \pm 0.01 \text{ mm}$.

Sintering of the compacts was carried out in a resistance furnace at a high temperature regime: a heating rate – 10 dg/min , temperature – 1600°C and isothermal holding time – one hour cooling with a furnace.

Treated non-plasticized plasma chemical NP Al_2O_3 was consolidated using the SPS method in the device SPS-515S (Sumitomo). Sintering mode is shown in table 3.

Table 3. SPS mode.

Composition	Pressure (MPa)	Holding time (min)	Sintering temperature (°C)
NP Al_2O_3	40	5	1400

Spark plasma sintering (SPS) is considered to be a promising effective method of consolidation of powder materials [6, 7]. Compared with traditional methods of consolidation of powder materials such as furnace sintering and hot pressing (HP) SPS allows to obtain high density sintered materials at a lower temperature for a short time of isothermal holding.

After SPS samples were cylinders with a diameter $15.0 \pm 0.1 \text{ mm}$ and a height of $2.0 \pm 0.2 \text{ mm}$. The density of sintered samples ρ was determined by using hydrostatic weighing in 96% ethanol with an accuracy of $\pm 0.001 \text{ g}$. The relative density of the samples Θ was also calculated.

Microhardness was determined with a help of the device PMT-3, hardness HRA – with a stationary Rockwell hardness tester, the load was 1000 mN (100 g).

The study of technological properties according to the above techniques showed the almost complete absence of flowability and very low bulk density of oxide NP. Coarse-dispersed powders Al_2O_3 have a satisfactory level of characteristics presented in the table 4.

Table 4. Technological characteristics of initial powders.

No.	Powder composition	Bulk density, (g/cm^3)	Tap density, (g/cm^3)	Flowability, (g/s)
1	NP Al_2O_3	0.07	0.06	-
2	NP 80% Al_2O_3 -19% ZrO_2 -1% Y_2O_3	0.14	0.14	-
3	Coarse pure Al_2O_3	1.47	1.65	0.4
4	Technical alumina	1.50	1.66	0.4

Thus, the study of plasma-chemical properties of NP Al_2O_3 suggests practical impossibility of their use in the initial state for the corundum ceramics technology.

The results of sieve analysis of the initial coarse-dispersed oxide powders are presented in table 5. It can be seen that the powders have a similar fractionated distribution of particle.

Table 5. Granulometric composition of the coarse-dispersed powders.

Particle fraction	Content of fraction X, %	
	Coarse pure Al_2O_3	Technical alumina
+025	0	0
-025+020	1.0	3.3
-020+016	6.1	4.2
-016+0125	9.6	10.1
-0125+008	15.3	13.8
-008+0063	24.0	23.8
-0063+0045	23.9	24.6
-0045	20.1	19.8

To improve technological characteristics plasma-chemical and coarse-dispersed powders based on Al_2O_3 were activated in a planetary mill for 20 minutes at the rotation frequency of grinding vessels – 30 Hz. This mode is optimum for oxide powders to treat [8]. The data are given in table 6.

Table 6. Technological characteristics of treated powders.

No.	Powder composition	Bulk density, (g/cm^3)	Tap density, (g/cm^3)	Flowability, (g/s)
1	NP Al_2O_3	0.82	1.23	0.2
2	NP 80% Al_2O_3 -19% ZrO_2 -1% Y_2O_3	0.95	1.26	0.2
3	Coarse pure Al_2O_3	1.22	1.47	0.4
4	Technical alumina	1.36	1.49	0.4

During the treatment spherical particles of plasma chemical powders were failed and united in hard agglomerates. Processing of coarse-dispersed powders Al_2O_3 significantly increased the content of fine fractions (-0063) – up to 60%.

The most effective mode of mechanical activation of the white electrocorundum powder in a planetary ball mill Activator 2SL was defined: the rotation frequency of grinding vessels f – 30 Hz, time of treatment – 40 min. During the treatment by this mode there was practically no coarse-

dispersed fractions (+010), the content of medium sized fraction was reduced (-010 + 008) and the output of fine fraction (-0063) was significantly increased – more than 75% (table 7). Bulk density of the treated powder was 1.23 g/cm³.

For further experiments the Al₂O₃ powder of pure alumina grade had been eliminated since the properties of corundum ceramics sintered from this powder have been investigated in detail in [9].

Table 7. Granulometric composition of the white electrocorundum (the rotation frequency of grinding vessels f – 30 Hz).

Particle fraction	Time of treatment, min			
	10	20	30	40
	Content of fraction X, %			
+020	0.5	0.1	0	0
-020+014	4.4	2.5	2.1	0
-014+010	2.2	2.1	2.0	1.4
-010+008	18.5	14.4	9.7	10.1
-008+0063	8.8	13.3	12.6	13.3
-0063+0045	53.7	51.4	48.8	47.7
-0045	11.8	16.2	24.8	27.5

Treated powder compositions 1, 2 and 4 (table 6) and the powder of white electrocorundum were dispersed on a fraction –0063 and mixed with activating additives in a planetary mill at the rotation frequency of grinding vessels f – 30 Hz for 40 minutes. Then the mixture was plasticized according to the procedure described above. Compositions of obtained powder mixtures are given in table 8.

Table 8. Compositions of powder mixtures.

No.	NP Al ₂ O ₃	Composition, wt. %			NP Al	TiO ₂
		NP 80% Al ₂ O ₃ - 19% ZrO ₂ -1% Y ₂ O ₃	Technical alumina	White electrocorundum		
1	100	0	0	0	0	0
2	95	0	0	0	5	0
3	98.5	0	0	0	0	1.5
4	0	100	0	0	0	0
5	0	95	0	0	5	0
6	0	0	100	0	0	0
7	5	0	95	0	0	0
8	10	0	90	0	0	0
9	20	0	80	0	0	0
10	0	0	95	0	5	0
11	0	0	98.5	0	0	1.5
12	0	0	0	100	0	0
13	10	0	0	90	0	0
14	0	0	0	95	5	0
15	0	0	0	98.5	0	1.5

Compacts were obtained from these mixtures by sintering under the given above modes. Dependencies of density and microhardness of the ceramics sintered from the technical alumina powder on the content of NP Al₂O₃ additives are shown in Figure 1. Adding NP Al₂O₃ in the technical alumina increased density and microhardness of sintered ceramics. This activating effect can be explained by the increase of the area of interparticle contacts which is caused by the adding of NP Al₂O₃. The mechanism of sintering activation due to increased structural and surface activity of NP

Al_2O_3 which can be defined by the crystalline structure defects, size and shape of particles. The most significant increase in density was observed in the ceramics containing 5...20 wt. % of additive NP Al_2O_3 .

In this paper, experiments were conducted to study the influence of the NP Al additive on a structure and physico-mechanical properties of ceramics sintered from NP Al_2O_3 . The problem of additional contribution to the activation of NP Al_2O_3 sintering by adding of NP Al is of a practical interest. Decrease in density of sintered ceramics was revealed when adding nanosized aluminum to the NP Al_2O_3 . This, in turn, led to decrease in hardness of the samples (Figure 2).

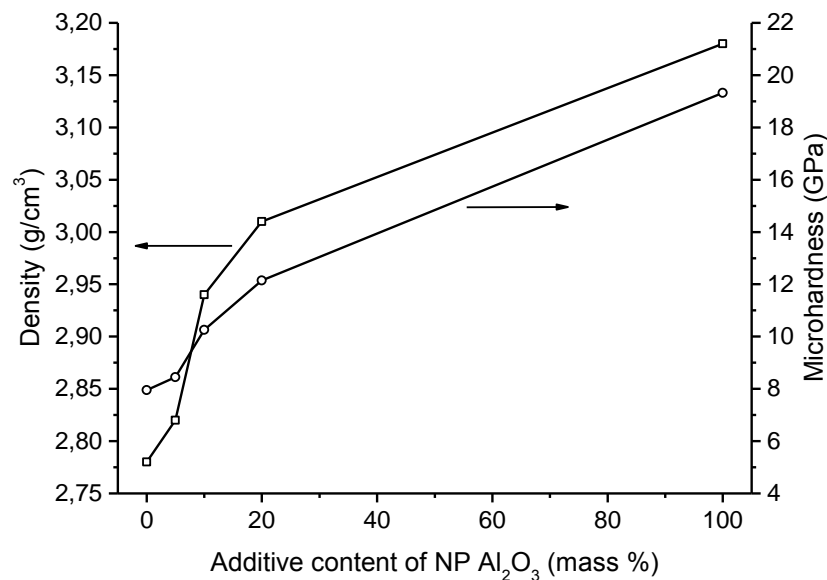


Figure 1. Dependence of the density and microhardness of alumina sintered from the coarse-grained powder Al_2O_3 of a technical alumina type on the additive content of NP Al_2O_3 .

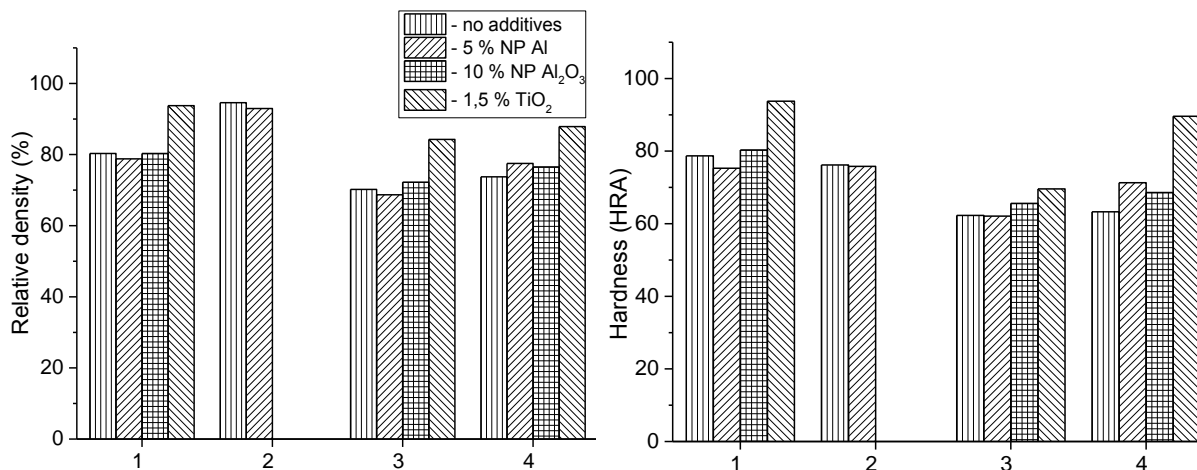


Figure 2. Dependence of relative density and hardness of ceramics on the content and chemical composition of additives: 1, 2, 3, 4 – ceramics sintered from NP Al_2O_3 , NP 80% Al_2O_3 -19% ZrO_2 -1% Y_2O_3 , technical alumina and white corundum, respectively (for composition (1) the first and third columns are equivalent, for composition (2) NP Al_2O_3 and TiO_2 powder have not added).

Such dependencies can be explained by the increased porosity of sintered ceramics due to oxidation of the additive of Al NP to α -Al₂O₃ during sintering. The oxidation was accompanied by greatly reduced specific volume of a final product of the added additive caused significant difference density of Al (2.7 g/cm³) and α -Al₂O₃ (3.96 g/cm³) that has been observed in some experiments.

The density of corundum ceramics obtained by consolidation of the treated unplasticized, plasmachemical NP Al₂O₃ by the SPS method made 3.63 g/cm³ (92% of theoretical density α -Al₂O₃), hardness – 93 HRA.

The greatest activating effect had the additive of TiO₂ in the Al₂O₃ powder. The density of the sintered ceramics containing 1.5 wt. % TiO₂ reached 3.48 g/cm³. The partial substitution for Al⁺³ by Ti⁺⁴ ions caused oxygen vacancies. It should be noted that the number of atoms in the unit cell of the crystalline lattice of the solid solution TiO₂ in α -Al₂O₃ was reduced. It also confirms that the TiO₂ forms a solid solution of subtraction in corundum. The crystalline lattice of a solid solution of subtraction has increased diffusive ability, and thus activates the sintering of corundum.

3. Summary

It is shown that adding the nanopowder Al₂O₃ to the content of 20 wt. % to the coarse-dispersed powders α -Al₂O₃ of grades technical and white alumina activated a sintering process of corundum ceramics that led to increase in its relative density and hardness from 70.2 to 72.2% and from 62.3 to 65.6 HRA for technical alumina, and from 73.7 to 76.5% and from 63.3 to 68.6 HRA for white alumina.

The activating influence of adding of Al nanopowder in the coarse-dispersed powder of α -Al₂O₃ on the sintering process was not revealed. When adding of nano-dispersed Al in the NP Al₂O₃ decrease in the density and the hardness of sintered ceramics due to the additive oxidation up to α -Al₂O₃ was observed. This led to reduced specific volume of the final product of the added additive caused by significant difference of Al and α -Al₂O₃ density, and decrease in density of sintered ceramics. In doing so, the main advantage of NP additive as sintering activator was not implemented, it is the possibility to form a large number of interparticle contacts at very low its content in a sintered compact.

The efficiency of SPS method to obtain dense corundum ceramics from the investigated powders is proved. The greatest activating effect had the adding of TiO₂ powder (1.5 wt. %) in corundum powders. During sintering it is formed a solid solution subtraction of TiO₂ in α -Al₂O₃, the lattice of which has a high diffusivity and activates sintering process.

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