Activated sintering of ceramics on the basis of Al_2O_3

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Abstract. Ceramic sintering on the basis of Al_2O_3 activated by nanopowder additives Al_2O_3 and Al has been studied. The given paper shows that adding nanopowder Al_2O_3 in the amount of up to 20 wt. % into the coarse powder α-Al_2O_3 activates the sintering process and, as a result, leads to the increase in density and microhardness of sintered alumina ceramics. The study has revealed a significant effect of alumina ceramic density growth which is due to introducing the submicron powder TiO_2 to the initial blends composition.

1. Introduction

The most widespread methods of obtaining strong alumina ceramics are powder techniques, i.e. various types of pressing and sintering modified as applied to ceramics. Nevertheless, the complexity and poor performance by hot and hot isostatic pressing techniques [1, 2] that make it possible to obtain materials with maximum high structural characteristics [3] handicap a wide practical application of strong alumina ceramics. As a rule, a relatively simple technique of uniaxial pressing followed by free sintering does not allow obtaining ceramics with a high level of mechanical properties [4]. Therefore, the problem of activating processes of alumina ceramic consolidation is of great practical importance.

This work aims at investigating the activating methods of ceramic sintering based on Al_2O_3 through powder mechanical processing in a planetary mill adding nanopowders (NP) Al, Al_2O_3 and submicron powder TiO_2 into a blend and applying the technology of spark plasma sintering (SPS).

2. Experiment

Manufactured oxide nanocrystalline powders (NP) Al_2O_3, Al_2O_3 - ZrO_2 - Y_2O_3, obtained by plasma-chemical synthesis were used. Besides plasma-chemical NP, coarse pure aluminum oxide powder, technical alumina powder and white electrocorundum were applied in the work. The electro-explosive NP Al was used as an activating additive.

Particle size analysis of the coarse pure Al_2O_3 powder and technical alumina was conducted with the help of the analyzer A 20. Powder test portions with a weight of 50 gr were taken; vibration motor frequency was 70 Hz with sizing time 10 min. After sizing the fractions were weighed and the percentage of each fraction was calculated. Also bulk density, tapping density, flowability of all the powders under study were determined.

Oxide powders were annealed in air in a high-temperature resistance furnace at 1450°C for an hour to transform γ-Al_2O_3 into α-Al_2O_3.

To improve the processing characteristics and to increase activity, the annealed powders were processed in the high-energy planetary ball mill for 20 minutes at the rotation frequency of the grinding vessels 30 Hz. Zirconia balls were used as grinding bodies.

In order to determine the activating effect of machine processing on the consolidation process, white electrocorundum was machined at various modes (the rotation frequency was *f* – 20 and 30 Hz with processing time τ – 10, 20, 30 and 40 minutes at each frequency).

On being treated, the powder blends were sieved through the sieve No. 0045 for 10 minutes on the vibration motor C.1 to obtain fractions < 45 μm and plasticized by carboxymethylcellulose (CMC) water solution in an amount of 5 wt. % CMC – 95 % of the powder.

After granulation and drying, the plasticized powders were molded by uniaxial pressing method in a steel mold, extrusion pressure was 400 MPa. The obtained compacts had the form of cylinders with a diameter of 10±0.01 mm and a height of 5±0.01 mm.

Compact sintering was carried out in a high-temperature resistance furnace according to the following mode: heating rate was 10 deg/min, isothermal holding temperature was 1600°C with time 1 h, cooled with the furnace. The processed unplasticized plasma-chemical NP Al_2O_3 was consolidated by means of SPS method in the unit SPS-515S (Sumitomo).

The specimens sintered by SPS method had the form of cylinders with a diameter of 15,0±0,1 mm and a height of 2,0±0,2 mm.

The density of the sintered specimens ρ was determined by hydrostatic weighing method in 96% ethanol (ρ_{et}=0,807 g/cm^3 at 20°C) with an accuracy of ±0,001 g. Also, the relative density of specimens Θ was calculated from:

$$\theta = \frac{\rho}{\rho_t} \cdot 100\,\%,$$

where ρ_t is the theoretical density of ceramics.

The analysis of processing characteristics according to the abovementioned methods has shown that oxide nanopowders have a very low bulk density and flowability is substantially absent. The coarse powders Al_2O_3 possess a satisfactory level of processing characteristics. The data are presented in table 1.

Table 1. Processing characteristics of initial powders.

No.	Powder composition	Bulk density, (g/cm^3)	Tapping 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

The electro-explosive NP Al has bulk density equal to 0,2 g/cm^3 and it does not possess flowability.

Thus, the analysis of plasma-chemical NP Al_2O_3 properties allows making a conclusion that it is practically impossible to apply them in their initial condition as ready-to-use process feedstock.

table 2 shows the results of particle-size analysis of the initial coarse oxide powders. It indicates that the powders have a similar fractional particles distribution.

Table 2. Grain-size composition of coarse powders.

Particles fraction	Fraction composition 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 the processing characteristics of plasma-chemical and coarse powders on the basis of Al_2O_3, they were processed in a planetary mill for 20 minutes at the grinding vessels rotation frequency of 30 Hz. Such a mode of oxide powder processing is optimal [5]. The data are presented in table 3.

Table 3. Processing characteristics of machined powders.

No.	Powders composition	Bulk density, (g/cm^3)	Tapping 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 processing, spherical particles of plasma-chemical powders were destroyed and grouped into hard agglomerates. The processing of coarse powder Al_2O_3 significantly increased the composition of fine fractions (-0063) up to 60%.

It has been found that the most effective mode for processing white electrocorundum powder in the planetary ball mill is as follows: the rotation frequency of the grinding vessels should be f – 30 Hz with the processing time τ – 40 min.

When powders are processed according to this mode, coarse fractions substantially disappear (+010), the number of medium fractions reduces (-010+008) and fine fraction outcome significantly increases (-0063) to more than 75% (Table 4). The bulk density of processed white electrocorundum powder was found to be 1.23 g/cm^3.

Table 4. Grain-size composition of white electrocorundum powder (grinding vessels rotation frequency f was 30 Hz).

Particles fraction	Processing time, min 10	 20	 30	 40
	Fraction composition 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

Figure 1 shows the diagrams of extruding powders without activating additives which were processed in a planetary mill and plasticized. These studies were conducted to determine the optimal extrusion pressure. It can be observed that when the pressure exceeds 400 MPa, the increase in pressed density is quite insignificant. Thus, the optimal extrusion pressures of the studied powders are within a range of 300 to 400 MPa.

Coarse pure Al_2O_3 powder was excluded from further experiments since the properties of the alumina ceramics sintered from this powder was analyzed by the authors in the work [6].

The processed powder compositions 1,2 and 4 (Table 3) and white electrocorundum powder were sieved into franction–0063, mixed with activating additives in the planetary mill. The mixtures were plasticized in accordance to the above method.

The compositions of the obtained powder mixtures are presented in table 5.

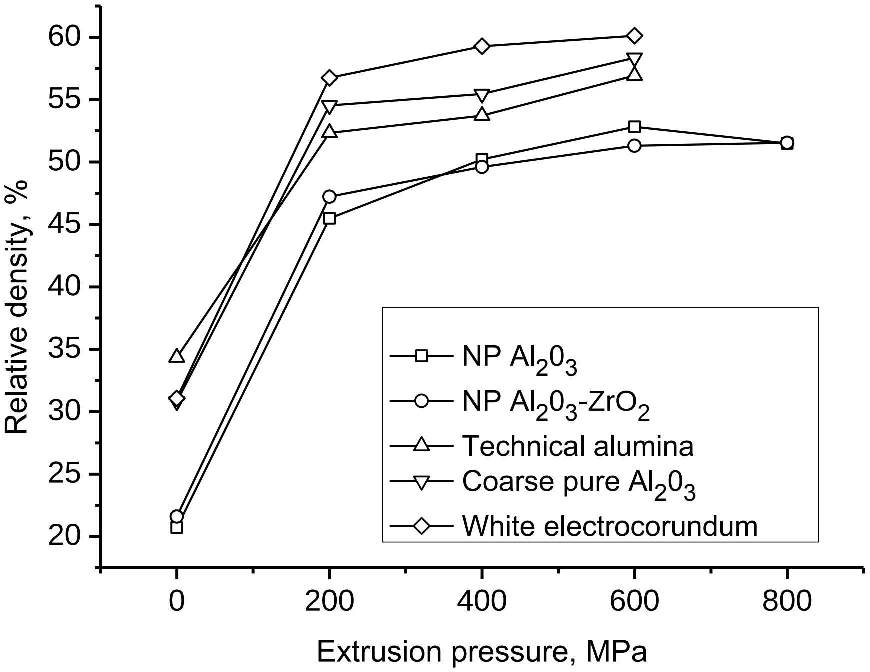

Figure 1. The diagrams of extruding the processed oxide powders (the grinding vessels rotation frequency is *f* – 30 Hz with the processing time τ – 40 min).

Table 5. Powder mixture compositions.

No.	Composition, wt. % NP Al_2O_3	NP 80% Al_2O_3-19% ZrO_2-1% Y_2O_3	Technical alumina	White electrocorundum	NP Al	TiO_2
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

The prepared mixtures were used to obtain a compact sintered according to the above modes.

Figure 2 shows the results of measuring the density ratio of the sintered alumina ceramics. Adding NP Al_2O_3 into technical alumina powder increased the density of sintered ceramics. This activating effect is due to the expanding area for particle contacts which results from adding NP Al_2O_3. The sintering activation mechanism is due to the increased structural and surface activity of NP Al_2O_3, which is determined by the crystal structure faultiness, the size and shapes of particles. The most considerable growth in density was observed in the ceramics containing NP additive Al_2O_3 in an amount of 5 to 20 wt. %.

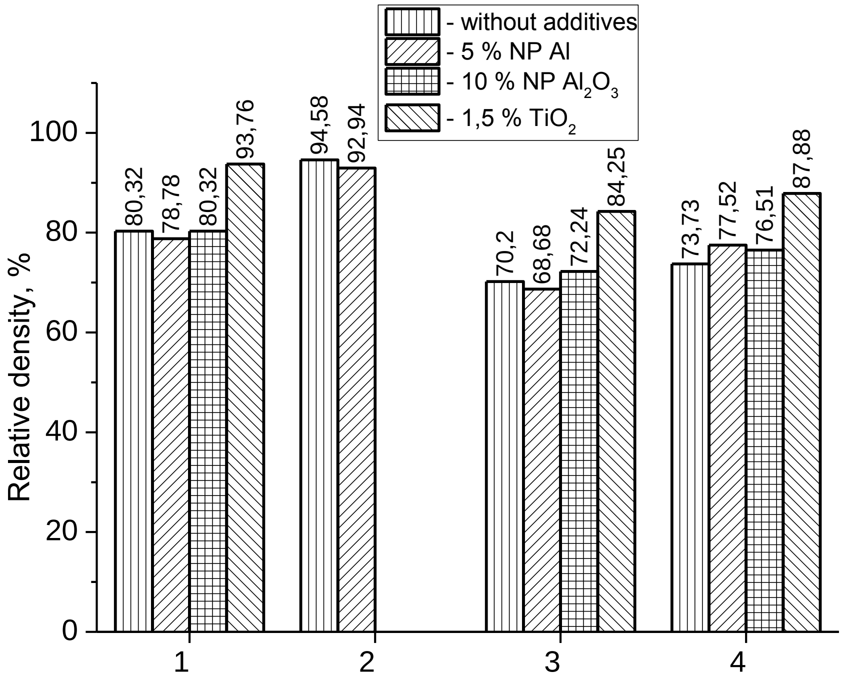

Figure 2. The dependence of ceramic density ratio on the additives amount and chemical composition: 1, 2, 3, 4 – ceramics sintered from NP Al_2O_3, NP 80% Al_2O_3-19% ZrO_2-1% Y_2O_3, technical alumina and white electrocorundum powders respectively (the first and the third columns are equivalent for the composition 1; NP Al_2O_3 and the powder TiO_2 were not added into the composition 2).

Additional contribution to activating sintering of NP Al_2O_3 owing to adding NP Al is the subject of practical interest. The reduction in the density of sintered ceramics was observed when nanodispersed aluminum was added to NP Al_2O_3. This is due to the increase in the sintered ceramic porosity caused by the oxidation of additive NP Al up to α-Al_2O_3 within the sintering process. The oxidation was accompanied by a significant decrease in the specific volume of introduced additive caused by a significant difference in density of Al (2.7 g/cm^3) and α-Al_2O_3 (3.96 g/cm^3) which was observed in a number of experiments. Thereby, the main benifit of NP as a sintering activator – its ability to form a great number of particle contacts at its very small amount in the sintering compact – turned to be unimplemented.

3. Summary

Ceramic sintering on the basis of Al_2O_3 activated by nanopowder additives of Al_2O_3 and Al has been studied. It was shown that adding nanopowder Al_2O_3 up to 20 wt. % into the coarse powder α-Al_2O_3 activates alumina ceramics sintering process. Consequently, there is an increase in density and microhardness of the sintered alumina ceramics. The research has indicated a significant effect of alumina ceramic density growth resulted from introducing the submicron powder TiO_2 in the amount of 1,5 wt. % into the initial blends composition.

References

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