Structure formation of hot pressed Al_2O_3 powders under the alternating electric current: experimental observations

Edwin Gevorkyan[1], Sergiy Lavrynenko[2], Miroslaw Rucki[3*]

[1]Materials and Manufacturing Technology for Transport Applying Products Dept., Ukrainian State University of Railway Transport, pl. Feyerbaha 7, Kharkov, 61010, Ukraine
[2]Information Technology & Systems KGM Dept., National Technical University "Kharkov Polytechnic Institute", Frunze Street 21, Kharkov, 61002, Ukraine
[3]Faculty of Mechanical Engineering, Kazimierz Pulaski University of Technology and Humanities in Radom, Krasickiego Street 54, Radom, 26-600, Poland

[*]Corresponding author, Tel: (+48) 483617696; E-mail: m.rucki@uthrad.pl

Received: 15 March 2017, Revised: 19 March 2017 and Accepted: 09 April 2017

DOI: 10.5185/amlett.2017.1718
www.vbripress.com/aml

Abstract

The paper presents the results of investigations on hot pressure sintering under the alternating current. The powders of different grain sizes were used for the sintering to investigate the impact of the powder on the final sintered structure and relative density. The additional experiments were focused on the kinetics of the Al_2O_3 nanopowders sintering. They confirmed that the time of the process duration is dependent on the temperature and the applied pressure. However, compared to the powders of tungsten monocarbide, it depends on the temperature rise speed in rather small degree. Discussion of the results pointed out that the obtained data, both theoretical and experimental one, confirmed possibility that during the sintering process the dislocations might appear and spread. It seemed reasonable to assume that in the low voltage regime the activated sliding with diffusion accommodation prevails, while in the high voltage regime the dislocation creep does.

Keywords: Nanopowders, sintering, ceramics, compaction.

Introduction

Highly dense corundum ceramics [**1**] perform high strength, hardness, wear resistance, heat resistance and high corrosion resistance [**2**]. In many cases, practical applications prefer non-porous material with small grain steady crystal lattice. The optimal conditions of temperature and pressure for fabrication of such a ceramic based on Al_2O_3 were proposed [**3**], but they did not consider the ceramics grain size, which is important from the performance characteristics perspective.

It is commonly known that the grain growth is dependent on the pressing time, pressure and temperature. High pressure and low temperature provide smaller grains, especially when the time interval is short. Investigations on the pulse electric current sintering were reported [**4**], as well as spark plasma sintering, high pressure sintering and rate controlled sintering [**5**]. Practical verification of these advantageous technologies, however, has exposed problems like large residual porosity, stable pores in triple junctions, defective grain boundaries and intensive grain growth.

The authors of the current project worked out the equipment for hot pressing with directly applied alternating current of the frequency 50 Hz, able to obtain the current of 10,000 A with voltage of 8-10 V. This apparatus was used for the experimental research on the sintering process and its effects. Despite the shorter sintering time at lower temperature, the process still left substantial grain growth, which inspired further investigations.

Today many ceramic materials can be produced in a form of nanopowders with particle sizes below 100 nm [**6**]. The process of high temperature pressing (electric consolidation) of the dielectric nano-dispersed powders with the directly applied electric current is not known well. Among others the questions rise on the structure forming processes and the high temperature sintering of the dielectric refractory powders. Some studies revealed the crucial role of the bonding effect on the mechanical behavior of the compacts [**7**], other point out the importance of number of touching neighbors for each particle, known as the coordination number [**8**]. However, despite the numerous investigations of the consolidation processes of various nanodispersed powders using the Field Activated Sintering Technique (FAST) [**9**, **10**], the

main peculiarities of their electric sintering are still not understood in full.

The following paper presents the results of investigations on hot pressure sintering under the alternating current using the powders of different grain sizes. The attempt was made, based on the achieved experimental data, to reveal some basic laws ruling the structure forming of the nanodispersed powders Al_2O_3 with the particle sizes ca. 60-80 nm produced by the company Infarmat (USA).

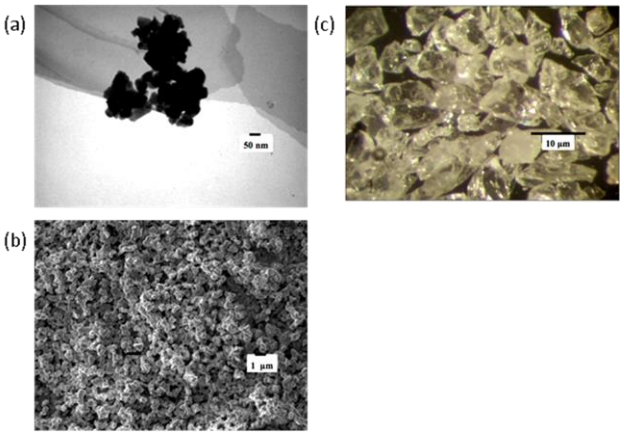

Fig. 1. Initial powders $A1_2O_3$: (a) 0.056 μm, (b) 0.6 μm, (c) 7 μm.

Methodology of the research

The effect of particle size of the powder on the densification behavior was reported for the tungsten components powders from 0.4 to 7.0 μm [**11**]. In the present study, ceramic samples were made out of the aluminum oxide powder Al_2O_3 of dispersity 7 μm, 0.6 μm and 0.056 μm. **Fig. 1** presents the photos of all three types of the applied powders.

Table 1. Grain size of the sintered samples of $A1_2O_3$ made out of different powders.

No	Initial powder [μm]	T_{max} [°C]	P [MPa]	t, [min]	T_{start} [°C]	T_{end} [°C]	ρ/ρ_t	grain size [μm]
1	6-7	1380	45	2	1100	-	0.965	8-10
2	6-7	1200	45	2	1100	-	0.71	7-8
3	0.6-0.7	1350	45	2	1000	1280	0.98	1-2
4	0.6-0.7	1380	45	2	1000	1280	0.99	1-2.5
5	0.6-0.7	1220	45	2	1000	-	0.825	1-1.5
6	0.6-0.7	1110	45	2	1000	-	0.76	0.8-1.2
7	0.056-0.06	1250	45	2	800	1150	0.995	1-3
8	0.056-0.06	1150	45	2	800	-	0.994	0.2-0.4
9	0.056-0.06	1130	45	2	800	-	0.993	0.2-0.3

The density of the obtained sintered samples was measured with the hydrostatic weight method in water. The analysis of the powder structure before sintering, as well as the examination of the broken surfaces of tested sintered samples, were performed with the scanning electron microscope (JSM-840).

The powders were first prefabricated as a tablet of a diameter 20 mm and weight 4 g. In the hot-pressing process, the high density small grain graphite powder was applied (MPG-7 type) with the maximal pressure 45-50 MPa. For that pressure, the temperatures of the beginning (T_{start}) and the end of the compaction (T_{end}) were determined by the displacement sensor and the acoustic emission measurement.

In the **Table 1,** there are described the conditions of the hot pressing of the $A1_2O_3$ powders with directly applied alternating electric current. The values of initial dimensions of the powder grain, obtained density and grain size after pressing are added, too.

Results and discussion

Fig. 2 shows the experimentally obtained graphs of the compaction versus temperature for different types of initial powder under the pressure 45 MPa.

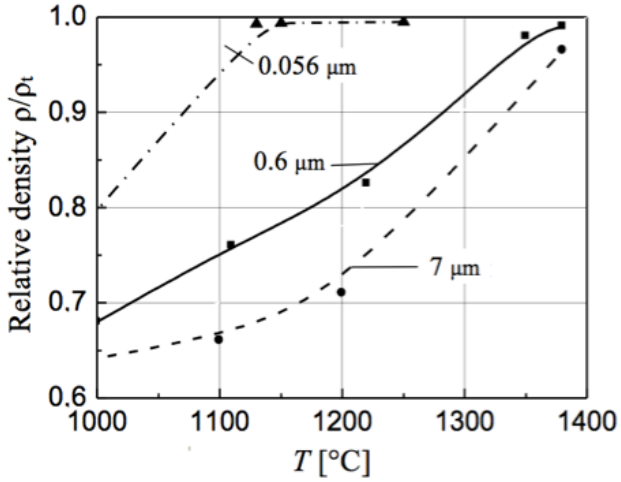

Fig. 2. Density versus pressing temperature at $P = 45$ MPa after $t = 2$ min.

It is obvious that the increase of the temperature leads to the density increase for all samples. Similarly, the density is higher for the samples made out of the initial powders of smaller grains. It is noteworthy that the powders of size below 0.06 provided the theoretical density values in $t = 2$ min at the temperature $T = 1130$ ºC, while the samples made out of the other powders (of 7 μm and 0.6 μm grains) reached the density close to 100% at the temperature $T = 1400$ ºC. Other recent studies report that the ceramic with 97.6% of theoretical density and 1.1 μm of average grain size was obtained at 1550 °C [**12**]. The samples made out of different size powders underwent the strength tests. The examples of the broken surfaces are presented in the **Fig. 3,** representing different stages of the compaction. As it was expected, the grains start to grow substantially at higher density.

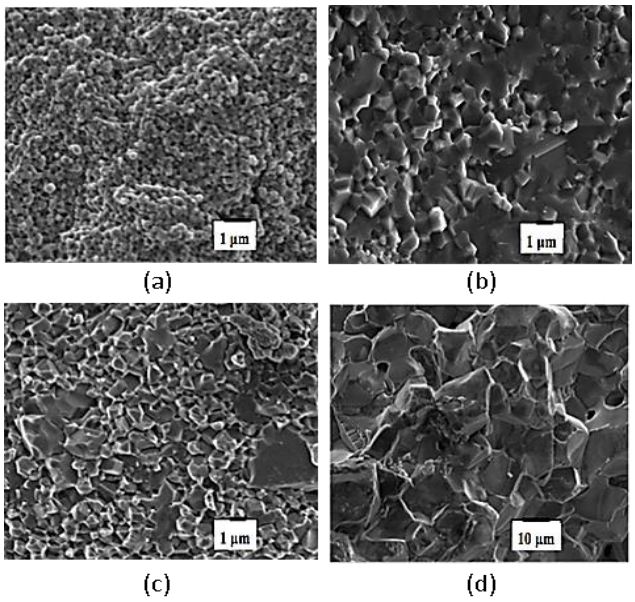

Fig. 3. Microstructure of the $A1_2O_3$ samples pressed out of the powders of different grain sizes (P=45 MPa, t=2 min): (a)0.056 μm at T=1130ºC, ρ/ρ_t=0.994; (b) 0.056 μm at T=1250ºC, ρ/ρ_t=0.995; (c) 0.6 μm at T=1380ºC, ρ/ρ_t=0.990; (d) 7 μm at T=1380º C, ρ/ρ_{reop}=0.965.

The correlations between the grain dimensions and the relative density for all examined samples are presented graphically in the **Fig. 4.** Typically, all of them reveal grain size growth at higher values of density.

It is seen, however, that in case of the 7 μm and 0.6 μm powders the graph rises steadily **(Fig. 4b and c),** while the nanopowder of 0.056 μm performs quick grain growth at the density close to 100%. Additionally, it should be noted, that the compaction in case of the hot pressing with directly applied alternating current for the nanopowders takes place at the temperatures generally lower. As it is seen from the **Table 1**, T_{start} is of 200 and 300 ºC higher for the powders of 0.6 μm and 7 μm grains, respectively.

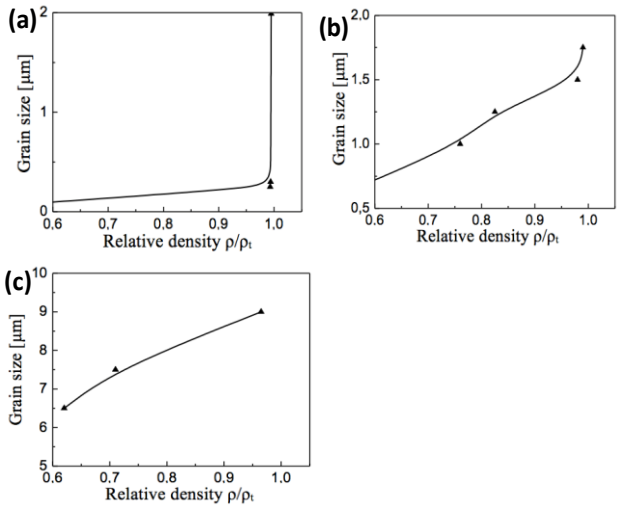

Fig. 4. Grain sizes obtained after hot-pressing under voltage of the different powders: (a) 0.056 μm, (b) 0.6 μm, (c) 7 μm.

Nanopowder compaction process

The additional experiments were focused on the kinetics of the Al_2O_3 nanopowders sintering. They revealed that the time of the process duration is dependent on the temperature and the applied pressure. However, compared to the powders of tungsten monocarbide, it depends on the temperature rise speed in rather small degree. The graphs presented in the **Fig. 5** illustrate this phenomenon.

One of the main forces driving the consolidation process, apart of the excessive surface energy, is the energy of the grains dividing boundaries. When the temperature rises, there appears the physical contact between the particles. Then the ramified system of the boundaries appears on expense of the free surface energy, while the excessive energy plays the role of the sintering motor. Quick heating forces the particle to slide on the surface of one another along the boundaries, and this way the sample density quickly increases. The sintering process is activated also by the energy of the lattice imperfectness, which is of substantial value in the nanopowders produced by plasma chemical technique.

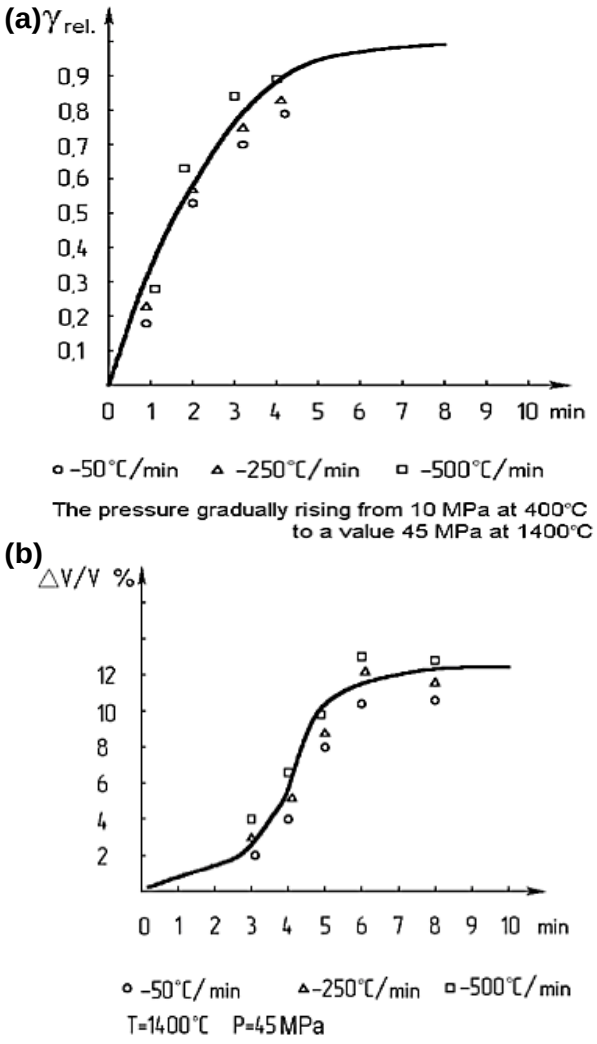

Fig. 5. Increase of the relative density of Al_2O_3 (a) and its volume (b) at different speed of heating.

It is known that during the sintering process, appears and increases the contact between the particles. According to some authors [**13**], the tensions in the connection of two sintered particles are dependent on the particles dimension. It is described by the following formula:

$$\sigma = 4\gamma x + 12\pi r\gamma / x^2 + 4\pi r\gamma \quad (1)$$

where:
σ – the voltage of the surface tension;
γ – free surface energy;
r – radius of the grain;
x – intersection surface of the contact area between the sintered particles.

Since the free surface energy is exceeding the boundary energy, the energies of the vacant formation on those two surfaced differ between one another. Supersaturation of the vacant places is different on the free surface of the neck and on the boundaries between the particles. The gradient of the vacant concentration determines diffusion mass transfer towards the neck. Kinetics of the contact surface growth between the particles is described by the formula [**14**]:

$$x^{\omega} = A(T)\, t \quad (2)$$

where:
x – contact surface between the particles, mm^2;
A(*T*) – function dependent on the temperature, particles geometry and the mechanism of the mass transfer;
ω – exponent.
If the mass transfer is performed according the mechanism of the surface self-diffusion, the formula will take the following form:

$$x^7 = 28\gamma\Omega D_s \delta_s r^3 / RTt \quad (3)$$

where:
x – contact surface between the particles, mm^2;
γ – free surface energy, kJ/mm^2;
Ω – vacant volume, mm^3;
D_s – surface diffusion coefficient;
δ_s – thickness of the surface diffusion layer, mm;
r – radius of the grain, mm;
R – gas constant;
T – temperature, °C;
t – time, min.

In fact, the growth of the boundaries takes place simultaneously because of the volume diffusion, surface diffusion and the diffusion along the grain boundaries. Using the Johnson's methodology [**13**] for the description of the sintering considering volume diffusion, surface diffusion and the diffusion along the grain boundaries, with the experimental data it is possible to find out the corresponding coefficients of the diffusion. The mechanism of the diffusion-viscosity assumes that the grain boundaries represent the sinks for defects. However, in that model, the role of the linear defects is omitted. In the nanodispersed particles, the dislocations usually are bound to the surface.

The obtained data, both theoretical and experimental one, confirmed possibility that during the sintering process the dislocations might appear and spread [**15**]. Thus, it is reasonable to assume, that the nanoparticles contain the linear defects in considerable amounts. The limitations of the dislocation reproduction in each small particle do not exclude its possibility for the group of the particles, where the source of the dislocations lays in the contact plane. Here, the dislocations may appear during the sintering process in the contact area between the single grains.

Conclusion

The performed researches and theoretical analyzes led to the conclusion, that it is possible to obtain the sintered structure with grain size under micrometer only when the undesirable grain growth is slowed down. This is the necessary condition for the obtaining of nanostructured material.

The results of investigations suggest, that in order to obtain the density close to the theoretical value but with minimal grain size, the hot pressing with the directly applied alternating current should be performed in strictly controlled time span. In practice, that means rather slow rise of the temperature to 900 ºC (full outgassing), and then quick heating from 900 up to 1150 ºC. The material should be exposed to the maximal temperature shorter. It is acceptable to add some substances to slow down the grain growth, like yttrium oxide, magnesium oxide, zirconium dioxide, tungsten monocarbide etc. It is crucial, however, to mix them steadily in the Al_2O_3 powder.

It is reasonable to assume that in the low voltage regime the activated sliding with diffusion accommodation prevails, while in the high voltage regime the dislocation creep does. In case of the high-speed sintering under the high temperature pressing, under conditions of the directly applied alternating current to the conducting graphite mold, in the nanodispersed powders of Al_2O_3, most probably take place both of the mechanisms, which enables to achieve the density close to the theoretical value even at the temperature 1100°C. It could be compared with the standard sintering process with the quick heating of the sub-micron Al_2O_3 powder, where the density of 94.7% may be achieved only at the temperature 1850°C after 10 minutes. Quick heating in the sintering provides slow kinetics of the grain growth in the pure aluminum oxide, with minimal increase of the grain size.

Acknowledgements

This work was not supported by any specific fundings.

Author's contributions

Conceived the plan: EG, SL; Performed the expeirments: EG, SL; Data analysis: EG, SL, MR; Wrote the paper: SL, MR. Authors have no competing financial interests.

References

1. Bai, J.; Yang, X.; Xu, Sh.; Shi, Y.; Yang, J.; *Scripta Materialia*, **2013,** *68*, 393. **DOI:** 10.1016/j.scriptamat.2012.10.054
2. Hnatko, M.; Tatarková, M.; Galusková, D.; Sedláček, J.; Bystrický, R.; Lenčéš, Z.; Šajgalík, P.; *Corrosion Science*, **2016**, *109*, 230. **DOI:** 10.1016/j.corsci.2016.04.007
3. Gevorkyan, E.S.; Shkuropatenko, V.A.; Chishkala, V.A.; *High Technologies of Machine-building: Printed scientific works KSPU "KhPI"*, **2006**, *13*, 20 (in Russian). **DOI:** not available
4. Leon, C.A.; Rodriguez-Ortiz, G.; Nanko, M.; Aguilar, E.A.; *Powder Technology*, **2014**, *252*, *1*. **DOI:** 10.1016/j.powtec.2013.10.025
5. Ragulya, A. V.; *Advances in Applied Ceramics*, **2008**, *107*, 118. **DOI:** 10.1179/174367608X318844
6. Champion, Y.; *Powder Metallurgy*, **2008**, *51*, 125. **DOI:** 10.1179/174329008X284912
7. Langlois, V.; Jia, X.; *Powder Technology*, **2011**, *208*, 509. **DOI:** 10.1016/j.powtec.2010.08.051
8. German, R.M.; *Powder Technology*, **2014**, *253*, 368. **DOI:** 10.1016/j.powtec.2013.12.006
9. Wang, S.W.; Chen, L.D.; Hirai, T.; *J. Mater. Res.*, **2000**, *15*, 982. **DOI:** 10.1557/JMR.2000.0140
10. Zavaliangos, A.; Zhang, J.; Krammer, M.; Groza, J.R.; *Mat. Sci. Eng. A*, **2004**, *379*, 218. **DOI:** 10.1016/j.msea.2004.01.052
11. Mamen, B.; Song, J.; Barriere, Th.; Gelin, J.C.; *Powder Technology*, **2015**, *270A*, 230. **DOI:** 10.1016/j.powtec.2014.10.019
12. Sun, Zh.; Li, B.; Hu, P.; Ding, F.; Yuan, F.; *Journal of Alloys and Compounds*, **2016**, *688A*, 933. **DOI:** 10.1016/j.jallcom.2016.07.122
13. Johnson, D.L.; Quantitative determination of sintering mechanisms at primary and secondary stages, In Sintering theory and technology; Samsonov G.V. (Ed.), Naukova dumka: Kiev, **1974**, pp. 53-62 (in Russian). **DOI:** not available
14. Ashby, M.F.; Verral, R.A.; *Acta Metallurgica*, **1973**, *21*, 53. **DOI:** 10.1016/0001-6160(73)90057-6
15. Groza, J.R.; Risbud, S.H.; Yamazaki, K.; *J. Mater. Res.*, **1992**, *7*, 2643. **DOI:** 10.1557/JMR.1992.2643