

Electrical consolidation under pressure for Al_2O_3 and WC nanodisperse powders**

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The features of hot pressing by the method of electrical consolidation under pressure of nanodispersed powders of two types of materials—electrically conductive (WC) and nonconductive (Al_2O_3)—are considered. WC powder with a particle size of $<2 \mu\text{m}$ and $\alpha\text{-Al}_2\text{O}_3$ powder with a particle size of $<0.1 \mu\text{m}$ were used. The heating rate varied from 50 to 500 °C min⁻¹. Sintering was carried out in an electric field engendered by a direct current lead to the vacuum processing chamber, implementing the well known field-assisted sintering technique (FAST) with spark plasma sintering (SPS) on the original installation with longitudinal-axial pressing of the chamber contents. With rapid heating, the density of the sintered powders was 99% after 2 min exposure under a pressure of 40 MPa, reached at 1200 °C for Al_2O_3 and 1650 °C for WC. Grain size did not change significantly. Intensive compaction and minimal grain growth in each of these materials are caused by the combined effect of electric current and mechanical pressure, which favourably changes the mass transfer pattern, its intensity, uniformity and dispersion of the consolidated grain structure compared to conventional sintering, in which large grain growth is typical for both materials. The direct action of the electric current contributes to removal of impurities (contaminants from the surface) of the particles, activates their surface, changes the transboundary structure, provides direct physical contact between the grains, ensures cleanliness and flexibility of their boundaries, increases sensitivity to heat, intensifies their compaction, and alleviates the inevitable problem of shrinkage. High-speed electric heating of powders reduces the time of

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coalescence of grain boundaries, inhibits their growth and ultimately leads to the formation of fine homogeneous structures of high functionality.

Keywords: fine grain structure, high-speed electric heating, nanopowder, refractory ceramics, sintering

1. Introduction

The grain size during sintering of refractory ceramic compounds is largely determined by the heating rate. The imposition of an electric field and pressure allows the material to be quickly sealed while minimizing the grain size. High heating rate slows down grain growth. Rapid heating allows for rapid compaction and suppresses grain growth. These results were established, in particular, jointly at the University of California¹ and by ourselves.²

In the development of micro- and nanoprocessing technological approaches and their applications,³ we experimentally established successful dense sintering according to the method of electrical consolidation of fine powders under pressure;⁴ in particular, the temperatures of the onset of shrinkage for Al₂O₃ powders of different granularities in the micrometre, submicrometre and nanometre ranges were established (Table 1).

Table 1. Data for the electrical consolidation of Al₂O₃ powders under pressure (45 Mpa).⁵

Initial powder grain size/ μm	Sintering temperature/ $^{\circ}\text{C}$		Consolidated structure	
	At beginning of shrinkage	Max.	Rel. density	Grain size/ μm
6–7	1100	1380	0.965	8–10
0.6–0.7	1000	1380	0.99	1–2.5
0.056–0.06	800	1250	0.995	0.09–0.2

The present study was carried out with examples of refractory nonconductive (Al₂O₃) and electrically conductive (WC) materials and is devoted to experimental elucidation of the known general influence of heating rate on the compaction of powders, here applied to the technology of electrical consolidation under pressure.

¹ J.R. Groza and A. Zavaliangos, Sintering activation by external electrical field. *Mater. Sci. Engng.* **A287** (2000) 171–177.

² V.Yu. Kodash and E.S. Gevorkyan, *Tungsten carbide cutting tool materials*. US 6,617,271 (2003).

³ A.G. Mamalis, A. Markopoulos and D.E. Manolakos, Micro and nanoprocessing techniques and applications. *Nanotechnol. Perceptions* **1** (2005) 31–52.

⁴ E.S. Gevorkyan and Yu.G. Gutsalenko, Features and location of electrical consolidation by the direct action of alternating current during submicrometre- and nanopowder sintering under pressure. *Bull. NTU “KhPI”* **49** (2010) 144–161 (in Russian).

⁵ P.S. Kislyi, E.S. Gevorkyan, V.A. Shkuropatenko and Yu.G. Gutsalenko, Preparation of materials from aluminum oxide nanopowders using modern methods of consolidation. *J. Superhard Mater.* **32** (2010) 383–388.

2. Experimental conditions

Powders from reputable industrial manufacturers were used, namely: Al_2O_3 —with a particle size of $< 0.1 \mu\text{m}$ —produced by Sumitomo Chemical Co. (Japan); and WC—with a particle size of 50–70 nm—produced by Aldrich Co (Austria).⁶ Compactness of powders in the initial state of loading the sintering chamber averaged about 0.55 for Al_2O_3 and about 0.75 for WC. The commercial WC powder was 99% pure, with only traces of impurities present. The impurity composition of the Al_2O_3 powder is given in Table 2.

Table 2. Impurity composition of the $\alpha\text{-Al}_2\text{O}_3$ powder according to the supplier.

Element	Fe	Si	Mg	Cu	Na
Content (ppm)	9	150	10	<1	8

Loose powders were filled into graphite die-and-punch units with no additives or lubricants. The apparatus was equipped with a vacuum chamber, see Fig. 1. A vacuum of 10^{-2} Pa and uniaxial pressure of 45 MPa were used for all experiments.



Figure 1. Vacuum chamber of the hot-pressing apparatus (electrical consolidation).⁷

⁶ According to the mode of production, these powders can be classified—up to a point—either as *bulk nanoparticles* characterized by reproducible dimensional statistics due to the large *top-down processing* capabilities in relatively large-scale production facilities and, consequently, greater predictability of the technological results from subsequent sintering of the powders; or, in contrast, as experimental powder production of *engineered nanoparticles* in limited volumes, as was the case in some of our previous experiments, e.g. (for Al_2O_3) E.S. Gevorkyan, V.A. Chishkala and Yu.G. Gutsalenko, *Abstracts XXIV Conf. “Information Technologies: Science, Technique, Technology, Education, Health”* (Kharkov: NTU “KhPI”) **1** (2016) 95 (in Ukrainian); (for WC) M.K. Monastyrrov, T.A. Prikhna, A.G. Mamalis et al., Electroerosion dispersion-prepared nano- and submicrometre-sized aluminium and alumina powders as power-accumulating substances. *Nanotechnol. Perceptions* **4** (2008) 179–188. Note that the present article uses the terminological recommendations from NanoDictionary. *Nanotechnol. Perceptions* **1** (2005) 147–160.

⁷ M.O. Azarenkov, E.S. Gevorkyan, S.V. Litovchenko et al., *Device for hot pressing of powders by direct transmission of electric current*. Ukraine Patent 72,841 (2012) (in Ukrainian).

Under a voltage of 5–10 V, alternating currents up to 1500–2000 A were used, since alternating magnetic flux is more conducive to the uniform compaction of the powders during electrical consolidation. The powders were processed at heating rates of 50, 250 and 700 °C min⁻¹ up to 1200 °C (Al₂O₃) and 1650 °C (WC). The holding time in the final heating phase was 2 min.

Compacted samples were 19 mm in diameter and 5 mm in height. Sample densities were measured using Archimedes' method, with an error of less than 1%.

Phase analysis was carried out using a Scintag X-ray diffractometer XDS-2000 with monochromatic Cu K_α radiation. Microstructures of freshly fractured sintered samples were studied using an ISI DS 130 scanning electron ultramicroscope (SEM) at a voltage of 10 kV.

3. Results and discussion

It was found that WC shrinkage starts already at 600 °C. The density gradually increases with increasing temperature and reaches a maximum at 1650 °C. The final densities of the sintered compacts and the grain size of Al₂O₃ and WC are given in Table 3.

Table 3. Al₂O₃ and WC densities and grain sizes after sintering.

Rate of temperature rise/°C min ⁻¹	Real density after sintering/g cm ⁻³		Final grain size/μm	
	Al ₂ O ₃	WC	Al ₂ O ₃	WC
50	3.90	15.3	6–9	2–3
250	3.92	15.5	3–4	0.5–1
500	3.95	15.7	0.5–0.6	0.5–0.6

The process of sintering is accompanied by several auxiliary phenomena, the controlling parameters of which were fixed by us with the help of various tools and devices. Supervision of these phenomena and their changes when changing the main technological parameters allows us to operate the sintering process in the desired direction in order to receive materials with preset properties.

Refractory substances combine high hardness and elevated fragility. As a rule the shrinkage of preparations is accompanied by a reduction in the quantity of crystal structure defects, particle surface roughness and porosity, and by grain growth and general homogenization. It is possible to directly relate the process of sintering to only two phenomena: growth of the area of contact between particles and approach of the particle centres (i.e., shrinkage); other phenomena are indirect and secondary.

The explanation for the high processability of compaction of refractory and other nanopowders by hot pressing with direct electric heating should be sought in the physical features of the process. It is known that sintering moves a system consisting of separate particles to thermodynamic equilibrium; i.e., it is a process during which excess energy of the system decreases. One may assume that the energy of a free surface and its edges, and the defects of a crystal lattice, underpin the main driving force of sintering. The size of this driving force can be estimated from the sizes of the starting particles. For example, the specific surface of carbide

powders after milling is typically $1\text{--}5\text{ m}^2\text{ g}^{-1}$, and of powders made by plasm-chemical synthesis $10\text{--}40\text{ m}^2\text{ g}^{-1}$.⁸ In normal practice, a porosity of 40% is the result of practically any method for preparing material directly for sintering, whence it is an obvious inference that the excess energy is sufficient; it also performs the basic work of compaction, causing a flow of material into the voids. We join Kislyi et al.⁸ in admitting (with some approximation) that the flow of material to a surface with negative curvature is carried out under some effective pressure P_e caused by the surface tension:

$$P_e = 2\gamma r^{-1}, \quad (1)$$

where γ is the surface free energy and r the grain size. This pressure is large enough to bring nanodispersed particles together, where the pore size is comparable to the size of particles. Therefore, at least in the initial period of sintering of nanopowders, the pressure (1) causes a rapid compaction $\dot{\epsilon}$:

$$\dot{\epsilon} = AP_e^{\nu} \exp(-E_a R^{-1} T^{-1}), \quad (2)$$

where R is the gas constant and T the temperature, A and ν other constants, and E_a the activation energy; at the initial stage of sintering (creep mechanism) $P_e = P_{\text{creep}}$.

Along with excess energy, the energy of the grain interfaces, separating zones with different orientations from each other, also contributes to the force driving compaction. It is necessary to take into account that physical contact between pressed particles appears at the beginning of heating, when surface free energy is also expended for the formation of boundaries, the excess energy of which drives the sintering. Formation of the ramified system of boundaries is a result of thermally activated sliding along grain boundaries at the initial stage of sintering. Perfectly flat, small boundaries are formed between particles. With slow heating compaction proceeds very slowly until the sintering temperature is reached, which leads to grain growth. Contrariwise, as a result of fast heating, given the mechanism of thermally activated sliding along nanograin boundaries, and because the area of the interfaces is about an order of magnitude less than that of the nanopowder surface, further compaction proceeds much faster according to the characteristic equation (2), with $P_e = P_{\text{sliding}}$; $P_{\text{sliding}} \ll P_{\text{creep}}$.

The energy of crystal lattice imperfections also contributes to the driving force of sintering, accelerating the exchange of atomic positions:

$$n_a = n_o \exp(-E_{aad} R^{-1} T^{-1}), \quad (3)$$

where n_a is the number of atoms that have left their places in the lattice and occupied vacancies, n_o is a structural factor not dependent on temperature, and E_{aad} is the activation energy for annihilation of defects, whose value steeply declines in a damaged lattice. Therefore, it is necessary to severely break the structure for active compaction of a material, hence increasing n_a in eqn (3), e.g. by crushing, as occurs in nanopowders made plasm-chemically. If the lattice becomes more crystalline, the quantity of imperfections considerably decreases. So, for example, the diameter of coherent zones is $20\,000\text{--}50\,000\text{ nm}$ in WC with a specific surface up to $1\text{ m}^2\text{ g}^{-1}$, and this initial size becomes $200\,000\text{--}500\,000\text{ nm}$ after sintering at a temperature $0.8 T_m$, where T_m is the melting temperature.

⁸ P.S. Kislyi, N.I. Bodnaruk, I.O. Gorichok et al., *Physicochemical foundation of receipt of superhard materials*. Kiev: Naukova dumka (1986) (in Russian).

In addition, it can be assumed that electric discharges arise in zones of intergrain contacts at the moment of passing a sufficiently large electric current—5000–8000 A—which should cause plasma formation, which results in clearing and activation of the powder surface. In turn, clearing of the surface results in formation of pure grain boundaries and activation of the sintering process. For example, it has been shown that upon sintering Al nanopowders with a nonuniform layer of Al_2O_3 with a thickness of about 5 nm on the surface, this layer has been removed by the electric field and the powder was condensed up to the theoretical density;⁹ a pulsed current of high frequency was applied in that case.

Microstructures of Al_2O_3 and WC nanopowders hot-pressed in electrical consolidation mode are shown in Fig. 2.

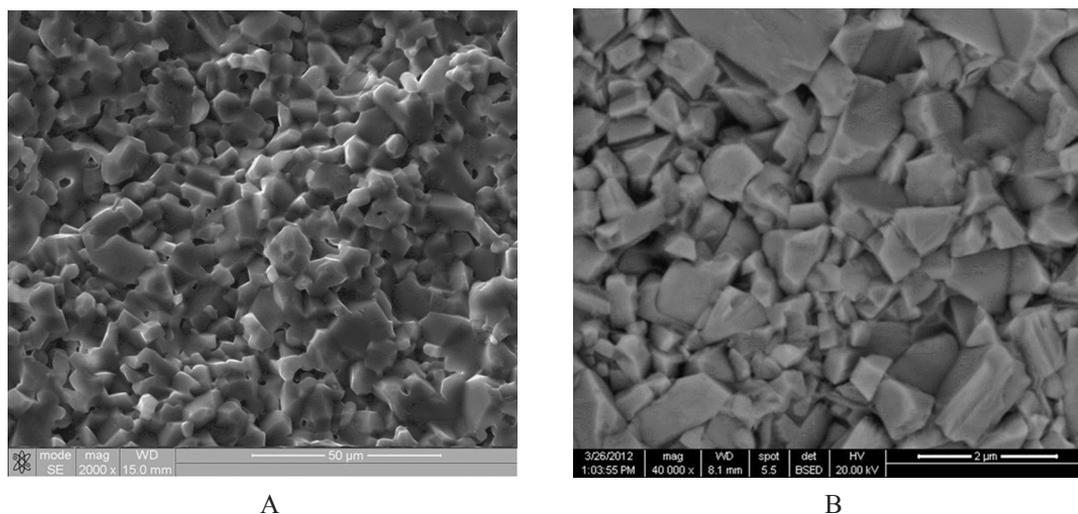


Figure 2. Scanning electron micrographs of sample fractures after sintering by electrical consolidation under a pressure of 40 MPa and holding at the maximum heating temperatures: A, Al_2O_3 (1200 °C); B, WC (1650 °C).

Electrical resistance is greatest in the places of local conductive contact of the powder grains at the initial stage of sintering. As a result, a significant amount of heat is generated. This allows the required temperature to be reached and inhibits grain growth for a short interval; we presume that catastrophic grain growth is not observed for this reason. For WC, the grain size was 5–6 times larger than in the initial powders at a heating rate of 700 °C min^{-1} ; 30–40 times larger at a rate of 250 °C min^{-1} ; and 60–90 times larger when heated at 50 °C min^{-1} . With the slowest temperature rise, the final Al_2O_3 grain size reaches 6–9 μm . For comparison, the grain size reaches 30 μm with ordinary sintering—up to 1850 °C—of pure Al_2O_3 with an initial grain size of 3–5 μm .¹⁰ Thus, it can be noted that the WC grain size largely depends on

⁹ J.R. Groza, Powder consolidation. In: *Non-Equilibrium Processing of Materials*, vol. 2 (ed. C. Suryanarayana), pp. 345–372. Oxford: Pergamon (1999).

¹⁰ J.R. Groza, J. Curtis and M. Kramer, Field assisted sintering of nanocrystalline titanium nitride. *J. Am. Ceram. Soc.* **83** (2000) 1281–1283.

the heating rate (Table 3). At the same time, the porosity changes insignificantly with increasing heating rate. In this case, rapid heating is particularly effective for suppressing grain growth. Sintering with a high rate of temperature rise slows down the diffusion transfer mechanisms, which generally have a strong influence on compaction.¹¹ Sintering at an increased rate lessens the flow of vacancies and suppresses large pores, and also limits grain growth.¹² The rapid decrease in porosity increases mobility at grain boundaries. This increases the sensitivity of fine, pure, electrically conductive powders to electrical heating during sintering.¹³

Rapid compaction in electrically nonconducting Al₂O₃ nanopowders likewise significantly reduces porosity and pore size. The mobility of grain boundaries and heat sensitivity increase accordingly.¹⁴ The number of small pores increases while large ones are suppressed. Small pores cause less interference with the mobility of grain boundaries, which favours compaction.¹⁵ In pure aluminum oxide with a low content of impurities, their effect on the mobility of grain boundaries is insignificant; it is determined mainly by the porosity. A high heating rate reduces the time needed to change grain boundaries and thereby reduces grain growth.

4. Conclusions

Our experimental studies lead us to conclude that final grain sizes very significantly depend on the heating rate when sintering WC and Al₂O₃ nanopowders. A high heating rate intensifies compaction and reduces grain growth. Electrical consolidation under pressure provides the means to carry out very short sintering cycles, typically less than 10 minutes for full densification of both conductive and nonconductive powders with grain sizes in the submicrometric and, especially, nanometric ranges. This yields opportunities to optimize energy consumption in the production of high-functional refractory materials and composites based on them.

¹¹ V.V. Skorohod, I.V. Uvarova and A.V. Ragulya, *Physicochemical Kinetics in Nanostructural Systems*. Kiev: Academperiodika (2001) (in Ukrainian).

¹² E. Gevorkyan, O. Melnik and V. Chishkala, The obtaining of high-density specimens and analysis of mechanical strength characteristics of a composite based on ZrO₂-WC nanopowders. *Nanoscale Res. Lett.* **9** (2014) 355.

¹³ E. Gevorkyan, Yu. Gutsalenko and N. Prokopiy, Effect of nanopowdered additions of tungsten monocarbide on properties of hard-alloy cutting material. *Fiabilitate Durabilitate* (Târgu Jiu) **1**(7) (2011) 1–6.

¹⁴ O. Scarlat, S. Mihaiu, G. Aldica et al., Enhanced properties of tin (IV) oxide based materials by field activated sintering. *J. Am. Ceram. Soc.* **86** (2003) 893–897.

¹⁵ E. Gevorkyan, S. Lavrynenko, M. Rucki et al., Ceramic cutting tools out of nanostructured refractory compounds. *Intl J. Refractory Metals Hard Mater.* **68** (2017) 142–144.