ELECTRIC SINTERING UNDER PRESSURE FOR MATERIALS OF INCREASED FUNCTIONALITY WITH REFRACTORY WEAR-RESISTANT BASIS

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ABSTRACT: *Results and features of refractory ceramics sintering from sub micro and nanocrystalline powders of* Al_2O_3, ZrO_2, *WC, SiC and others by electrical consolidation of powder composition under pressure that ensures obtaining of high-density materials of enhanced mechanical functionality including competitive abilitied in tool applications are considered.*

KEYWORDS: aluminum trioxide, zirconia, tungsten carbide, silicon carbide, spark-plasma sintering. ceramic composites, cutting tools, heat resistance, hardness, strength.

1. INTRODUCTION

The leading determinants of the development of the technological platform of world civilization in the 21st century are, firstly, the four-connected trend concept "nano-bio-info-cogno" of the sixth technological mode, first announced in the USA at a seminar organized in December 2001 by the National Scientific Foundation in collaboration with the Department of Commerce and first published on-line in June 2002 [1]. Secondly, it is the program Industry 4.0 after announcement in April 2011 at the Hanover Trade Fair in Germany, which is considered by the European Union in the same dominant trending direction [2]. Thirdly, such is the program Society 5.0 which is adopted in January 2016 by the Cabinet of Ministers of Japan in the context of the transition to the highest level of development of human civilization in the chain of stages "hunting-agrarian-industrial-information-super smart" [3].

The rapid growth of volumes and the globalization of information flows in the industrial service of the requests of modern civilization aggravates competition and stimulates the search for breakthrough technical solutions in the interdisciplinary space of knowledge and practice, requires functional flexibility of professional intelligence and the materialization of its activities in accordance with the main trends in the development strategies of leading world economies.

The advanced development of applied intellectualization and the physical and technical platform of scientific activity in modern conditions is associated with the origin, perception and testing of non-obvious technical solutions in the spirit of the prospects for the development of technology and technology, the economy and society as a whole, outlined by trends [1-3]. The symbiosis of technology and nature in the context of trends [1-3] more and more goes beyond the scope of environmental problems and strives for mutually developing interaction, in-depth knowledge and expanded integration of the physical essence of natural phenomena in the advanced creative practice of human activity. Penetrating near-Earth space, natural electromagnetic fields and the electric discharge in these fields has played and continues to play one of the leading parties in the genesis of scientific and technological progress.

2. FROM INDUCTION TO DIRECT ELECTRIC HEATING

Starting from the crafts of the ancient Egyptians and Incas, powder metallurgy received mass application to the middle of the XIX century, after the development of a method for refining crude platinum and turning it into a malleable metal (1826, P.G. Sobolevsky and V.V. Lyubarsky) [4]. The successes of powder metallurgy in the twentieth century are mainly associated with the use of induction furnaces of a crucible design (1872 – the first device, 1900-1905 – the first plants for the production of ferrochrome, ferro-tungsten, ferrosilicon, A.N. Lodygin) [5].

The scientific and technical rivalry of the USSR and the USA in the second half of the 20th century, in particular the rapid development by both superpowers of rocket-space and nuclear-energy materials science, stimulated the appearance in the world practice of new high-strength and high-hard, heat- and wear-resistant materials, including those made from refractory ceramics for thermal protection of the hulls of the reusable spacecraft (Shuttle and Buran), the working chambers of nuclear reactors, the implementation of projects of high-power engines in ceramic design, etc. The development of an induction furnace [6], carried out in 1990 at the Institute of Superhard Materials of the National Academy of Sciences of Ukraine under the supervision of Academician P.S. Kislyi, is an example of a response to these challenges. This furnace allows to sinter large-sized products from refractory ceramics (ceramic rotor of a high-power gas turbine engine, etc.).

Industrial demands for high performance ceramics found a subsequent response in the technology of induction sintering of finely dispersed products from submicron and nanopowders. Further improvement of the structure of dense compositions based on refractory ceramics prompted a direct current supply to the sintered consolidate, which minimizes electrical losses for functional heating and allows for faster sintering cycles, thereby limiting grain growth in its process and forming structures of increased dispersion, as shown in the ascending to the scientific school of Academician P.S. Kislyi work [7].

A technological breakthrough in this direction is associated with the advent of spark plasma sintering (SPS) techniques and technologies in Japan, USA, Europe and then around the world, in which the main role is given to electric discharges and plasma in their channels in moving contacts and pores of consolidated structures of grain compositions [8-10]. Through the use of this technological approach, researchers of P.S. Kislyi – natives of the Institute of Superhard Materials of the National Academy of Sciences of Ukraine – were able to obtain unrivaled finely dispersed tungsten monocarbide structures [11]. P.S. Kislyi actively advised work on SPS and was directly involved in understanding their results and routing further research [12]. These works formed the basis of a retrospectively nearest decade related to the production and use of nano- and submicrostructures based on tungsten carbide, corundum, zirconia and other refractory materials and their composites.

3. MODERN ELECTRICAL SINTERING RESULTS

In modern experimental practice of direct electric sintering under pressure for nanostructured materials of increased functionality with a refractory wear-resistant base, here we highlight and briefly present some of our own and joint developments of the closest retrospective and current ones performed in the following directions:

– aluminum oxide ceramics (1);
– zirconium oxide ceramics (2);
– tungsten carbide ceramic (3);
– hard alloy ceramics on the basis of tungsten carbide (4);
– ceramic composites on aluminum oxide and tungsten carbide integrated base (5);
– ceramic composites on aluminum oxide and silicon carbide integrated base (6);
– ceramic composites on yttrium stabilized zirconium oxide base in combination with an aluminum oxide component (7);
– ceramic composites on yttrium stabilized zirconium oxide base in combination with a tungsten carbide component (8);
– ceramic composites on yttrium stabilized zirconium oxide base in combination together with aluminum oxide and tungsten carbide components (9);
– silicon-carbide-based ceramic composites with the addition of yttrium-stabilized zirconia in combination with an aluminum oxide component (10).

(1). Development of SPS aluminum oxide ceramics is much more advantageous in the sintering temperature of high density consolidates (97.6%) compared to not only the conventional process of the same stoichiometry (1130˚C versus 1550˚C) but also having a corresponding advantage, for example [13], before sintering ceramics from zinc sulfide (1360°C) or titanium dioxide (1200°C).

(2). We found that in the SPS method with nanosized powders of stabilized zirconia, the minimum thermal growth of grains in combination with their high compaction in a single solid (98%) is already ensured at a pressure of 30 MPa with a holding time of 5 min. at a maximum temperature of 1200°C. Moreover, in comparison with the closest analogue of purely mechanical technology, which requires exceeding the threshold of effective cold mechanical destruction of grain agglomerates (~ 300 MPa) and practically realized at a pressure of 400 MPa, SPS product has significantly higher mechanical characteristics, approx. 20% to microhardness and more than five times to compressive strength [14].

(3). In the above-mentioned work [13], the development of SPS of tungsten-carbide ceramics was also distinguished by a significantly lower dense consolidation temperature compared to the conventional stoichiometry process (1800˚C versus 2500˚C). Further improvement of the SPS cycle of tungsten-carbide ceramics allowed its implementation at 1650°C [15].

(4). SPS of the tungsten carbide-based hard alloys are represented here as a composition of the WC-Co group from a particularly fine-grained WC – 6 wt% Co mixture [16]. Compared with vacuum sintering, up to 30% increase in thermal conductivity, hardness and crack resistance is provided.

(5). This works are devoted to the sintering of nanoceramic materials with Al_2O_3 and WC joint participation in SPS of general consolidate which have special mechanical properties, with increased modulus of elasticity compared to conventional ceramics ("ceramic steel"), etc. [17]. The analysis of the physical properties of obtained ceramics revealed increased hardness and even some elasticity and increased flexural strength. Out of the nanostructured mixture of Al_2O_3 and WC powders in proportion 50–50%, the inserts for cutting tools were made. The comparative analysis of those inserts with the ones typically available in the market confirmed increased durability (up to 30%), as it had been expected [18].

(6). This group of ceramic composites is being developed from the perspective of a more affordable raw material alternative to high-speed tungsten steels (R18 with 18% W and others) and hard alloys in market competition with composite unions of aluminum trioxide and titanium carbide type VOK-60 (Aprelevka Plant of Technical Ceramics, Russia), HC1 or HC2 (NTK Ltd Co., Japan). As a result of SPS of integrally bimodal combinations of submicron (Al_2O_3) and nanosized (SiC) initial powders [19], we were able to obtain higher-hardness Al_2O_3 – SiC instrumental composites, which, moreover, are not inferior to these competitors or surpass them in thermal conductivity, see Table 1 with an example for Al_2O_3 – 15 wt.% SiC [20].

(7). Composites with the joint participation of ZrO2 and Al_2O_3 were obtained with increased strength and toughness compared to monocirconium or monocorundum ceramics [21].

Table 1: Characteristics for SPS composites of
Al2O3 – 15 wt% SiC and some competitors

Characteristic and unit of rating	Rating for:				
	R18	VOK-60	HC1	HC2	Al_2O_3 – 15 wt% SiC
Hardness, H_V, GPa	7.6	14.6	18.0	21.0	25.0
Thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$	22.1	15.0	17.0	21.0	23.0

(8). The structures of the compact ZrO_2 – WC system with a uniform density distribution and increased strength were obtained by hot pressing to T = 1350°C and P = 30 MPa with direct transmission of a large current by the SPS method [22].

(9). The direction continues the development of technologies in the trend (5), increasing the possibility of the effective use of ceramics in the aerospace industry [23], Table 2. The physic-mechanical properties of a typical conventional analog of Al_2O_3 - 40 wt.% TiC are inferior to the SPS received composite ceramics up to 30%.

Table 2: Characteristics for SPS composites of
Al_2O_3 – ZrO_2-3wt%Y_2O_3 – 50 wt% WC

Characteristic and unit of rating	Rating
Hardness, HRA (GPa)	92…94 (20…22)
Compressive strength, MPa	2600…2800
Bending strength (T = 20…900˚C), MPa	600…800
Thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$ at 22˚C (at 400˚C)	25 (40)
Young's modulus, Pa	400
Coefficient of crack resistance, K_{1c}, $MPa \cdot m^{1/2}$	12…15

(10). SPS of consolidates on the base of SiC with additives of aluminum trioxide and zirconium dioxide stabilized with yttrium (3 wt.% Y_2O_3) allows to obtain ceramic composites with high mechanical properties (H_V = 21.0 GPa, K_{1c} = 4-4.5 $MPa \cdot m^{1/2}$) [24].

The practice and development prospects for refractory ceramic composites with additives of conventional oxides deserve separate consideration. Currently, for example, the features and capabilities of ceramic composites in structures 60-80 wt% SiC – 15-30 wt% CuO – 5-10 wt% ethyl silicate. are in-depth investigated. After preliminary compaction under a pressure of 80-100 MPa, the composite charge is sintered at a temperature of 1400-1450°C to obtain a high-quality heat-resistant ceramic product of high electrical conductivity and thermal conductivity [25]. For example, for composite 60 wt% SiC – 30 wt% CuO – 10 wt%

ethyl silicate, corresponding properties are positioned in the ranges: electrical resistivity – 8-10 Ω ·sm, thermal conductivity, – 20-30 $W \cdot m^{-1} \cdot K^{-1}$. Moreover, resulting composites are distinguished by high mechanical characteristics: bending strength 600-800 MPa, hardness – 90-92 HRA, crack resistance, K_{1c}, 6-8 $MPa \cdot m^{1/2}$. Possible effective area of application – electrodes for resistance welding with high operational stability.

4. CONCLUSION

In our developments, we sequentially (see [14]) proceed from the well-known statement [26] that most of the properties of solids substantially size-dependent with a decrease in particle size to several interatomic distances in one, two or three dimensions. The production of refractory ceramics with high performance we associate with our own development of modern technological approaches [7] and equipment [27] for nanopowder metallurgy that goes back to the origins of the Japanese method of the SPS [8]. For the development of ceramic materials in the direction of ensuring a new level of technological heredity of production preparation of various articles thereof requires nanocrystalline ceramic powders with desired morphology, phase composition, the properties of the bulk phase and surface.

The studies performed on consolidates with a refractory wear-resistant base and their results presented here show that the synergy of dimensional and electrical (thermal and electric discharge) effects during sintering of nanopowders with their heating by direct supply of electric current and pressure is reflected in the range of materials with increased functionality and has the prospect of development. The capabilities of high-speed sintering provided by this technological approach increase the flexibility of developments in the trends of fast and energy-saving technologies. Limiting of grain growth by accelerated sintering supports the trend of nanostructured materials science solutions. The formed fine-grained structures correspond to the trend of increased readiness of powder metallurgy consolidates for increased mechanical loads.

DEDICATION

The authors dedicate this article to the memory of Academician of the NAS of Ukraine P.S. Kislyi (1933-2019) – outstanding citizen of Ukraine and a material scientist, the long light memory of which in human and professional senses have been prepared for with his whole life and work.

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