COMPOSITE MATERIALS FROM INDUSTRIAL WASTE BY SPARK PLASMA SINTERING METHOD

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ABSTRACT

This paper reviews the results of the processing of silicon and zinc industrial waste by spark plasma sintering method. Experiments on grinding and separation by size class of fractions of microsilica and zinc ashes were carried out. Industrial waste separated into different fractions was subjected to spark plasma sintering. Chemical composition and hardness of the obtained materials were determined. The microstructure of the obtained samples was studied. Obtained samples can be used in accordance with their complex of properties, namely, samples of zinc ash as conductive elements can be used in instrumentation, and samples of microsilica as dielectrics in aircraft construction.

Keywords: *spark plasma sintering, industrial waste, microsilica, zinc ash, ceramic material.*

INTRODUCTION

One of the problems of modern materials science is the search of new ways of industrial production waste recycling in order to obtain composite materials. Microsilica, a waste product from silicon production, is of a great interest in this direction.

However, the choice of methods for obtaining such materials is also a challenge. Promising is the use of modern technologies in the field of powder metallurgy, one of which is the innovative method of spark plasma sintering. In the Commonwealth of Independent States countries this method is known as electro-pulsed sintering under pressure, and abroad as spark plasma sintering. The main purpose of the spark plasma sintering method is high-speed sintering of powder materials of any nature to form new materials of a new type with unique compositions and properties, namely: thermoelectronic, optical, hard-alloy, composite materials, metal alloys, etc. [1]. The advantage of this method is the mechanism of sintering process itself, which is based on the principle of consolidation of powders in an electric field of direct current under the influence of a high-energy low-voltage pulse with power up to 100 kJ and constant mechanical load up to 30 tons. In places where pulses generate spark discharges between particles of sintered material, a large amount of thermal energy (Joule heat) is concentrated. This ensures local heating of powder particles to temperatures ranging from a few to tens of thousands of Celsius' degrees within a fraction of a second. This exposure results in partial melting, material evaporation, thermal and electrolytic diffusion and it results in sintering of the material [1].

In the spark plasma technology, the sintering of powder particles is carried out by the internal thermal energy of the material. This is the key difference from other sintering methods where necessary Joule energy is communicated to the material from outside, which requires many hours of holding. This method provides high rates of heating of the studied material (up to 200° min^{-1}), short holding time (a few minutes) of the sample at the final consolidation. It is known that high heating rates contribute to the removal of impurities on the particle surface (surface cleaning and activation), as well as limit grain growth and preserve the microstructure of the final sample (controlled porosity). In this case, a uniform distribution of heat over the sample regardless of the nature of sintered material is created by an electric current of the pulse type which allows obtaining multicomponent composite materials. The resulting new materials have a high density (up to 99.9 % of theoretical one), high homogeneity, and high strong bonds between the particles [1].

Since the method of spark plasma sintering has a number of advantages: uniform heat distribution over the volume of the sample, high density and controlled porosity, uniform sintering of single and dissimilar materials, short working cycle time; the universality of this method can be traced in many studies [2]. Herein, matrix composite materials from a mixture of tungsten carbide powders and brass (70 %) were obtained, which after spark plasma sintering have improved strength properties, wear resistance and structural density [3].

A powdered multicomponent alloy based on high-melting metals (W-Ta-Mo-Nb-V-Cr-Zr-Ti) is subjected to spark plasma sintering. It resulted in a conglomerate composite structure and improved strength properties [4].

Papynov et al. reported synthesis of a magnetic nanostructured ceramic with unique magnetic and strength properties on the basis of nanostructured hematite by spark plasma sintering, and a high-strength bioceramic with a bimodal porous structure similar to the texture of bone tissue promising for use in medicine was synthesized on the basis of nanostructured wollastonite [1].

Nanocrystalline alloy W-Ta (5 % Ta) was also obtained by the spark plasma sintering technology, resulting in a density of 95 % and a grain size of 1.73+1 μm [5].

Herein, ceramic materials were obtained on the basis of reactive purity oxides: MgO+g-Al_2O_3. Silica SiO_2 in the form of fine and nanodispersed powder used as a silica component. Ratio of input components MgO + g-Al_2O_3 + SiO_2 is 2 : 2 : 5 [6]. The resulting ceramic samples differed in dispersibility: when using a fine silica component, the crystallite size was 5 - 10 μm, and when using nanodispersed one was 1 - 5 μm.

Various methods of spark plasma sintering of Al_2O_3-ceramic workpieces for small-sized end mills are given in paper [7]. The initial component was high-purity powder a-Al_2O_3, sintering activators were not used.

Herein, a spark plasma synthesis was used to obtain ceramics based on nanodispersed silicon dioxide as a precursor of silica component of ceramic materials and based on silicon-alumina precursors of cordierite ceramics. It was found that the input of nanodispersed silica coagel into the blend significantly accelerates the formation process and improves the structural characteristics of the obtained ceramics [8].

The development of spark plasma sintering modes based on thermodiffusive flows of atoms arising due to local temperature gradients in the production of ceramic materials was carried out by the authors of paper [9]. As a result, a mechanism of spark plasma sintering based on accelerated diffusion was proposed and two stages of the process were considered: the thermodiffusion mechanism of ceramic framework formation during sintering and the thermodiffusion mechanism of pore healing during sintering.

In addition, it is shown how the method of spark plasma sintering of a dispersed precursor containing elemental iron, cobalt, and aluminum can be used to produce a compact sample with high hardness. It was proved that the high mechanical strength properties of the obtained compact sample are due to the formation of intermetallic compounds during sintering $FeAlFeAl_2$ [10].

Herein, a technology for obtaining powder materials of the Fe-N system by spark plasma sintering is proposed. Thus, the initial powder of crushed iron with a developed surface, reduced to almost pure iron, was subjected to nitriding in a vibrating fluidized bed in dissociated ammonia medium [2].

In addition, a method for obtaining products with complex shapes by the method of spark plasma sintering using quasi-isostatic pressing is proposed [11]. In the implemented developments, an electrically conductive mixture of graphites of different dispersions is used as a pressure transmitting medium: 1 mm graphite chips were mixed with P804T soot. Monolithic titanium hemispheres were used as the base of the workpiece. The research task was to apply a layer of porous titanium from a mixture of PTS grade titanium and sodium chloride to the outer surface of the base. The molds were made of graphite.

As can be seen from the conducted scientific and patent search, the method of spark plasma sintering has not previously been used to obtain materials from waste silicon and zinc production. Thus, recycling of waste silicon and zinc production in order to maximize the extraction of the relevant valuable components is proposed. Previous papers indicated that microsilica is one of today's best known pozzolanic substances and is actively used in the construction industry; it is a finely dispersed dust of gray color with amorphous properties [12, 13]. It is extracted from the off-gases of furnaces in the smelting of metallurgical silicon and ferrosilicon [14]. Microsilica, unlike traditional high-silica raw materials such as quartz sand, is a light finely dispersed material consisting of tiny spheres of amorphous silica with a particle size of 0.01 - 0.07 μm [15]. It is known that such amorphous microsilica (in its pure form) is used as filler and reinforcing agent for construction concrete [14]. In this paper the interest is directed into obtaining the crystalline phase from the amorphous phase (by spark plasma sintering) and its application.

Zinc ash (zinc slag) is a residue that forms in the galvanizing bath after galvanizing steel by hot dipping. After galvanizing, the zinc ash is removed after each galvanizing cycle [16].

EXPERIMENTAL

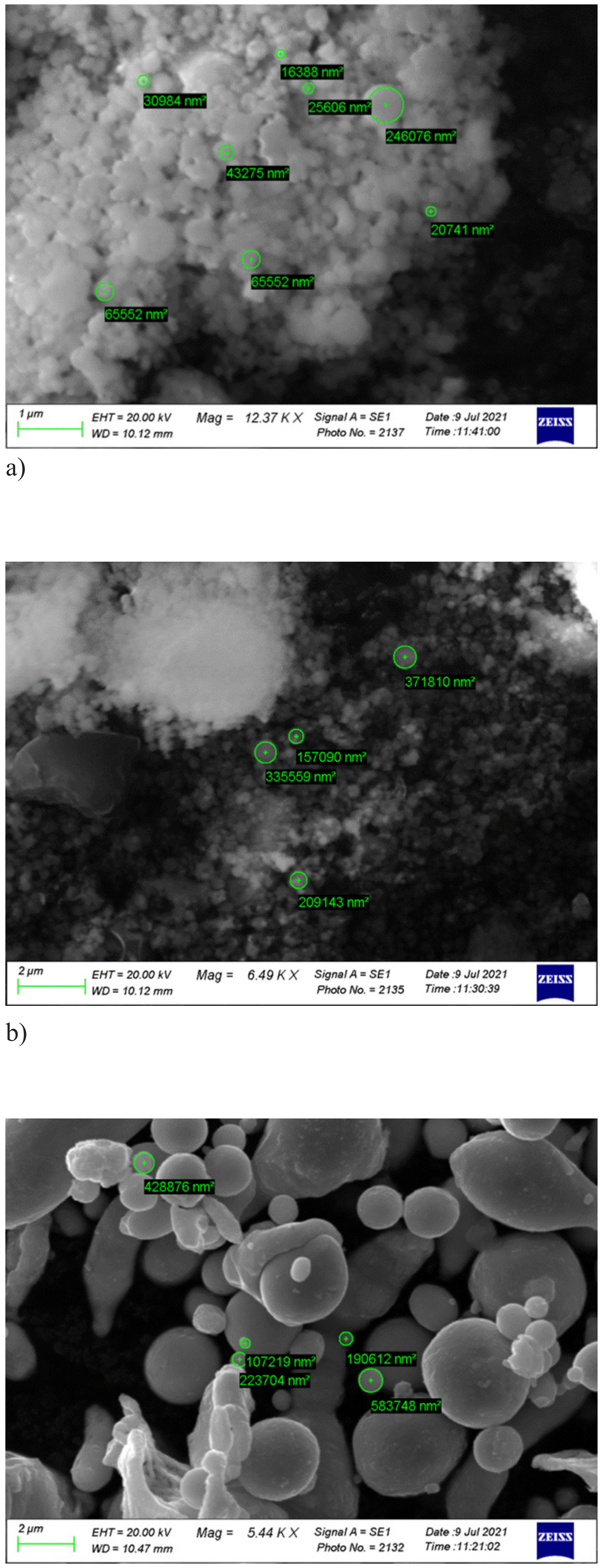
Microsilica powder weighing 100 g was divided into fractions of less than 45 (Fig. 1(a)) and 45-63 μm (Fig. 1(b)) on an analytical laboratory sieving machine "RetschAS200 control" [12, 13].

Then, the microsilica powder of fractions 45 - 63 μm and less than 45 μm was milled on an Emach high-speed ball mill in order to reach the nanosize level. Grinding speed was 1000 rpm, duration was 1 hour.

Waste zinc ash (Fig. 1(c)) was ground on a laboratory ball mill for 20 min. Then, the milled powder of these materials was separated into fractions less than 45 μm on an analytical laboratory sieving machine "Retsch AS200 control".

A study of the samples revealed that they contain particles of micro- and nano size.

The prepared sample powders were sintered in a spark plasma sintering unit. The process of spark plasma sintering is as follows: powder is poured into a mold, in which a vacuum of 10 - 2 torr is created, pressure of 50 - 100 MPa is applied by a punch and impulse voltage up to 3 kV which ensures current flow through the mold of up to 5 kA, the duration and frequency of current pulses are about milliseconds, temperature of spark



a)

b)

c)

Fig. 1. Microstructure of the studied samples: a - microsilica fraction less than 45 μm; b - microsilica fraction 45 - 63 μm; c - zinc ash.

plasma sintering is about 2000°C. When pulse current flows through the particles of powders to be treated, thermal effects occur: a) heating of the powder due to Joule heat; b) intense short-term spark discharge heating as a result of accumulation of electric charge of critical value between the particles of the powder. The powder is additionally heated from the molds and punches which also release joule heat when the pulse current flows.

RESULTS AND DISCUSSION

The sintering process and the resulting samples after sintering are shown in Fig. 2.

Table 1 shows the chemical composition of the samples obtained, determined by energy dispersion analysis.

According to Table 1, we can conclude that the spark plasma sintering of zinc ash produces metallic zinc, which is close to zinc grade Z3 (primary zinc) in terms of purity of extraction. This is explained that at high temperatures of SPS the burnout of impurities and vacuum outgassing of the sintered surfaces of the samples take place. The same effect occurs during processing of micro- and nanosilicas. In addition, the obtained materials are characterized by increased strength and density, as high rates of heating and cooling of the material during SPS contribute to the predominance of compaction processes over the diffusion mechanisms of grain growth, resulting in samples of high hardness. This is due to the absence of recrystallization process which unstrengthens the material.

Sintered samples were examined by X-ray phase analysis (Fig. 3). X-ray phase analysis of micro- and nanosilica (the images are identical) showed that as a result of spark plasma sintering the original crystalline and amorphous phases (observed in small amounts in nanosilica) when heated above 1470°C are transformed into a high-temperature polymorphic modification of quartz - crystabolite, trimidite was also identified (Fig. 3(a)). Cristobalite is a high-temperature cubic polymorphic modification of quartz formed when tridymite is heated above 1470°C and preserved as a metastable SiO_2 phase upon subsequent cooling. It can exist in one of two forms. High-temperature modification of cristobalite is cubo-hexa-octahedral β-cristobalite. It becomes metastable when cooled to 268°C, when it transforms into a low-temperature modification - tetragonal-tetrapezohedral α-crystobalite [17]. In the case of the sample obtained on the basis of zinc ash, X-ray phase analysis showed the presence of reduced metallic zinc as a result of such sintering (Fig. 3(b)).

Figs. 4 - 6 show the fracture microstructures of sintered materials, as well as their composition obtained by energy dispersion method. Fractures of microsilica < 45 μm and 45 - 63 μm after sintering are identical and present a microstructure of dense, homogeneous structure with melted walls, that is the initial microsilica

a)

b)

Fig. 2. Spark plasma sintering process (a) and obtained samples (b).

Table 1. Chemical composition of the studied samples.

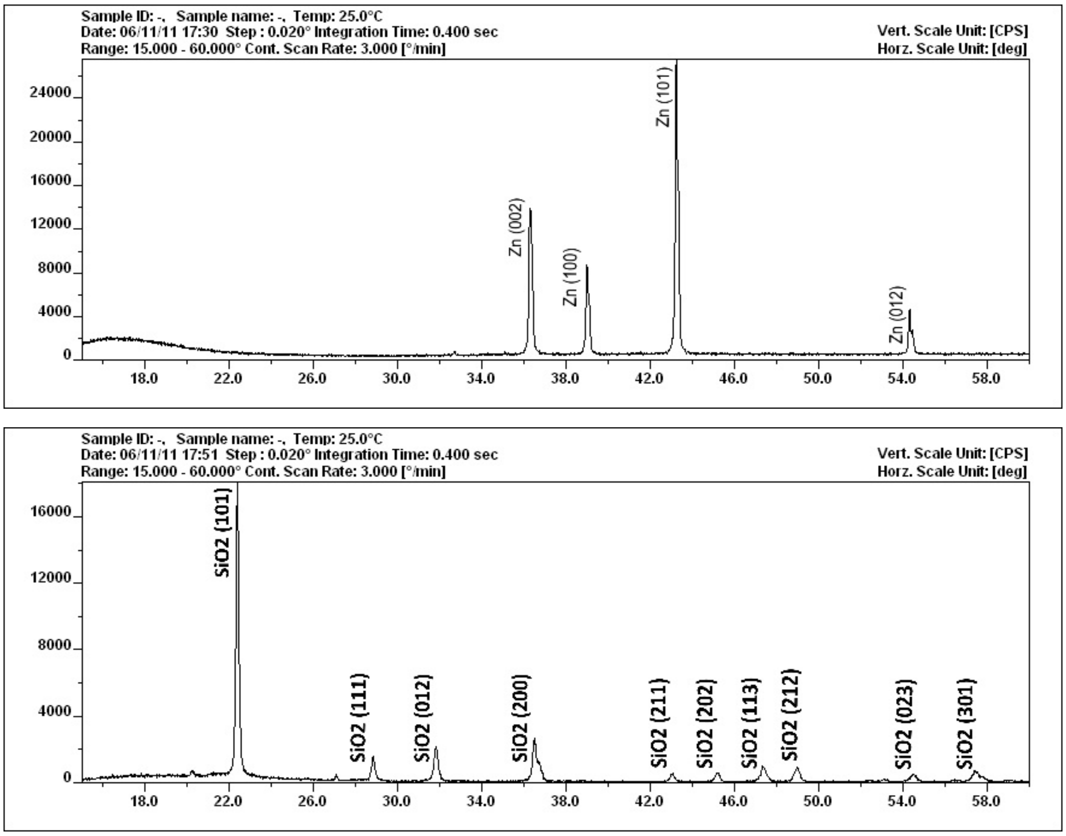
Element, %	Microsilica < 45μm	Microsilica 45 - 63 μm	Zinc ash, μm
Si	90.20	90.78	3.07
Ca	2.62	2.72	0.319
Sx	1.78	1,23	0.141
K	1.23	1.87	0.0518
Na	0.963	1.70	-
Al	0.936	0.571	0.477
Cl	0.749	-	-
Fe	0.604	0.295	0.172
Mg	0.285	0.382	0.290
Ba	0.213	-	0.0769
Mn	0.113	0.119	-
Px	0.106	0.170	0.0763
Ti	0.0684	0.0521	0.0707
Zn	0.0656	0.0310	94.16
Cr	0.0419	-	0.0170
Ni	0.0302	-	-
La	-	0.0826	-
Pb	-	-	0.264
Mo	-	-	0.234
Cs	-	-	0.148
Ru	-	-	0.139
Other indicators			
Hardness, HB	453.0	362.8	64.84
Presence of electrical conductivity	not present	not present	present

particles are well sintered (Fig. 4). The fracture is mixed (granular-porous).

The structure of sintered zinc ash is a dense, strong, porous conglomerate and consists of tightly adhering particles of rounded shape of nanoscale (Fig. 5). The fracture is granular.

Thus, composite materials based on microsilica obtained by spark plasma sintering have increased strength properties as a result of consolidation of the initial powder. Since the obtained samples are characterized by high strength properties, low weight (lightness) and lack of electrical conductivity, a possible area of application is dielectric elements in aircraft construction.

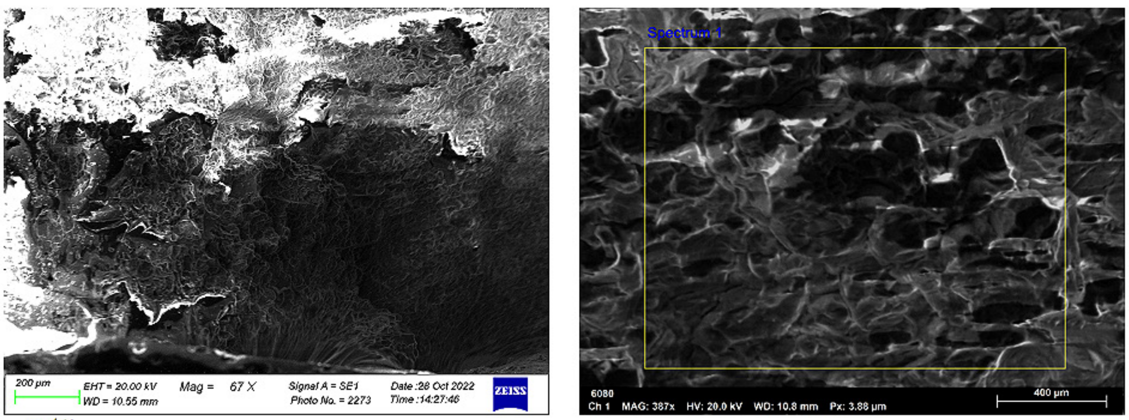
Zinc ash samples are characterized by plasticity which is associated with the reduction of zinc oxide, despite the consolidation of particles. A possible field of application could be instrumentation (e.g. as conductive elements).

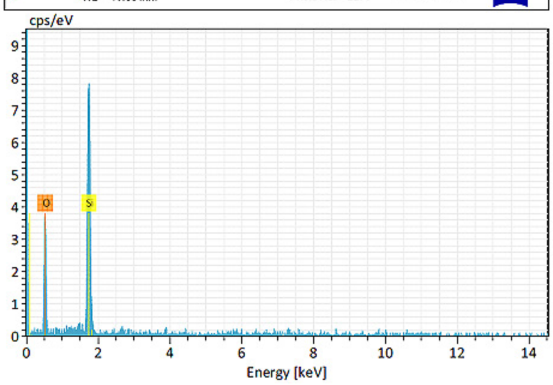


a)

b)

Fig. 3. X-ray phase diagrams: a - micro- and nanosilica, b - zinc ash.

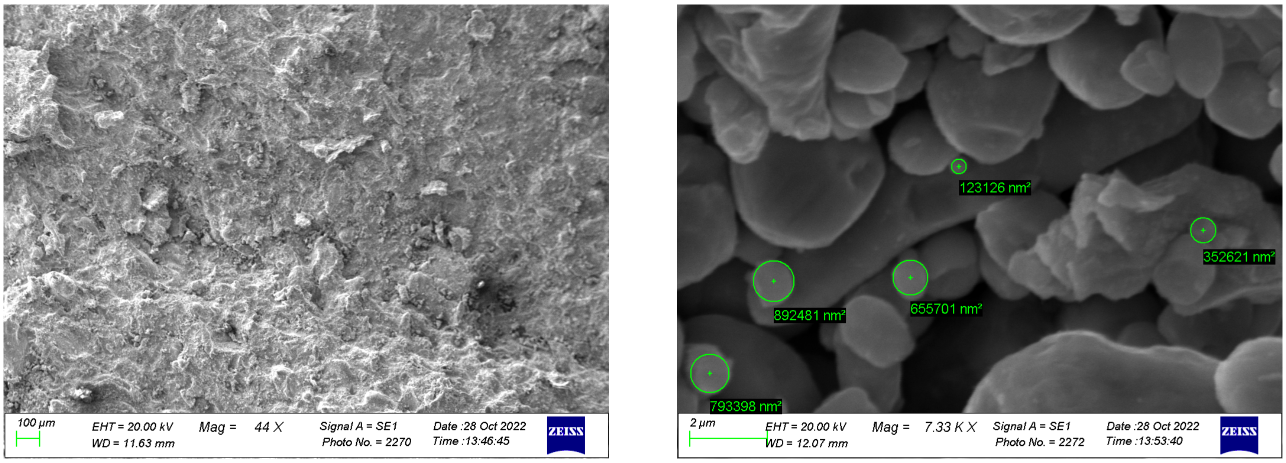




Spectrum 1

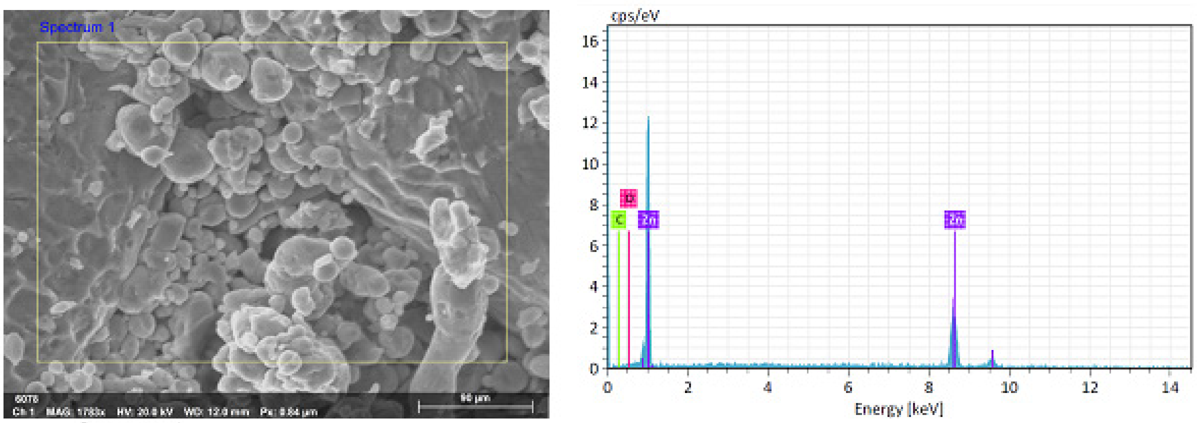
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Oxygen	8	1136	55.44	55.44	68.59	2.62	4.73
Silicon	14	4228	44.56	44.56	31.41	1.34	3.00
		Sum	100.00	100.00	100.00		

Fig. 4. Fracture microstructure and spectra of sintered microsilica.



a) b)

Fig. 5. Fracture microstructure of sintered zinc ash, a - 44x and b - 7330x, respectively.



Spectrum 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Zinc	30	7683	94.42	94.42	76.91	2.39	2.53
Carbon	6	98	4.08	4.08	18.11	0.25	6.01
Oxygen	8	122	1.50	1.50	4.98	0.10	6.62
		Sum	100.00	100.00	100.00		

Fig. 6. Microstructure and spectrum of sintered zinc ash.

CONCLUSIONS

The article describes the process and proves the principal possibility of using the method of spark plasma sintering for industrial waste recycling. Consolidated ceramics from silicon production wastes (micro- and nano-fractions), as well as metallic zinc extracted from zinc ash as waste from zinc production were obtained. The hardness values of the obtained materials are given. This proves the possibility of their further use in mechanical engineering, aerospace or as cutting ceramics, in case of hardening with other compositions. This effect is explained by the fact that the grains of sintered material by SPS method have a smaller size and are evenly distributed throughout the consolidated material, which in turn complicates the processing (cutting) of such hard materials. SPS as a method of industrial waste treatment makes it possible to obtain both current-conducting materials (metallic zinc) and dielectric materials in the case of microsilica.

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