Influence of technology of nanopowder production on the microstructure of the sintered by spark-plasma material on the example of aluminum oxide

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Abstract. A comparative study of the results of spark-plasma sintering (SPS) of two-types of aluminum oxide nanopowders, obtained by the method of conductor explosion and plasma synthesis. When the parameters of both powders are similar (spherical form of the particles, size, phase composition) as well as SPS modes the properties of the resulting compacts are significantly different both in mechanical properties and microstructure. The reason of differences in the properties of the obtained compacts is in technological impurities in powders, obtained by different methods. Artificial addition of impurities, contained in the nanopowder, obtained by electro explosion of conductor, into the powder, made by synthesis in plasma and not containing these impurities, allowed to reveal their effect on the formation of the microstructure and properties of the sintered by SPS method sample.

1. Introduction
Production of bulk materials by spark-plasma powders sintering having a nanostructure, allows to control formation of the microstructure of the sintered material and to achieve unique strength and special properties due to the short duration of the process [1-5]. At the same time a significant influence on the properties of the sintered material has a technology of obtaining initial nanopowder. For example, the presence of even very insignificant amounts of certain impurities can dramatically affect the properties of the sintered material and change the microstructure. The aim of this work is to study the causes of the formation of dissimilar structures of sintered by the method of spark-plasma using identical modes from nanopowders of similar properties but obtained in different ways aluminum oxides. The main focus of the work was placed on differences in the microstructure. All other properties were left behind the scenes.

2. Experimental equipment and methods
Two kinds of aluminum oxide nanopowder were used as an initial material for SPS:

1. The powder $\text{Al}_2\text{O}_3$, obtained by the explosion of aluminum wire in an oxygen-containing gas produced by “Advanced Powder Technologies”, Tomsk. According to the certificate the powder

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contains kappa, theta, and alpha phases, the traces of metal aluminum are present. Specific surface is 35-40 m$^2$/g. The arithmetic average size of particles is 36 nm, average size by surface – 46 nm, average mass size – 54 nm. Hereinafter – “powder 1” and sintered compacts “compacts 1”.

2. The powder Al$_2$O$_3$, obtained by oxidation of the disperse aluminum in air plasma of electric arc discharge [6, 7]. Delta phase dominates in the initial phase composition. Specific surface is 35,8 m$^2$/g close to the specific surface of the powder 1. Hereinafter – “powder 2” and sintered compacts “compacts 2”.

The form of particles in both kinds of powder is spherical what is proved by REM.

Spark-plasma sintering (SPS) of both powders was carried out in vacuum using LABOX-625 Sinter Land device in the graphite matrix with an internal diameter of 10 mm at a pressure of 50 MPa. Spraying of aluminum oxide was 0.4 g, which provided a height of the tablet slightly higher than 1 mm. Temperature was set and monitored using pyrometer. The heating rate was 100°C/min, maximum heating temperature – 1400°C, holding at max temperature – 10 min. This mode was obtained empirically, as a mode, providing high homogeneity at maximum average micro hardness on the surface of the sintered compacts.

Properties of compressed tablets were studied at different stages of sintering at normal temperature using a raster electron microscopy (REM TESCAN model VEGA). REM was carried out on tablets hear with spraying on it of platinum – palladium coating of thickness of a few atomic layers.

Semi qualitative analysis of micro impurities and compacts was carried out on time-of-flight mass spectrometer analyzer with lazed excitation [3-Nukleonika]. Both initial powders, pressed using a hydraulic press and microscopic sections of compacts, obtained from these powders by SPS were studied.

3. Experimental results
Microstructures of cross shears of tablets, obtained by the SPS of both types of powder are shown in Figures 1 and 2.

![Figure 1. Microstructure of the fracture of compact 1 (left) and compact 2 (right).](image)

It can be seen on the pictures that the compacts, obtained from the powder 1, in addition to the small grain areas have large grain areas of 300-500 microns. Such areas are absent in compacts obtained from powder 2, the microstructure is almost homogenous across the surface of shear. Deviations from the plane by the shear are caused by the destruction of the tablets (a blow with a sharp rod on the center of tablets).
Of particular interest are large grain areas. At high magnification, it can be noted that they are not simply composed of large grains but have a bimodal structure, consisting of a mixture of super-large (up to 40 microns) and ultrafine (0.5-1 microns) grains. (Figure 2)

This inhomogeneity of the structure, observed in compacts from powder 1, could be attributed to the poor quality of nanopowder and close the topic. However, mechanical test and measurements of micro hardness showed a significant excess of these characteristics not only over compacts, obtained from powder 2, but (at least in micro hardness) over literature data on corundum. In areas with bimodal structure micro hardness reached 35 MPa, instead of 20-24 MPa, specific to corundum or leucosapphire. This has stimulated the study of the causes of the observed anomaly.

Theoretically, at similar external parameters of particles of both powders they can vary in phase composition and by the presence of impurities. Aluminum oxide has a few low temperature modifications the ratio of which can be influenced by its production method. However, at temperature higher than 1200-1500°C all aluminum modifications proceed to a stable state $\alpha$-Al$_2$O$_3$. Sintering and formation of grains occur at temperatures which are higher than temperatures of this phase transition. Therefore, differences in the initial phase composition of the initial powders cannot influence the formation of the microstructure of the compact and properties. A more significant impact on the formation of the microstructure has to be expected from the presence of technological impurities.

Composition and approximate concentration of the impurities in four studied samples are given in the Table 1. Both powder samples and their compacts contain a lot of iron and silicon impurities (identification ambiguity is possible due to the undecidability of peaks Fe$^{+2}$ and Si$^{+4}$) and impurities of carbon and magnesium (peaks Mg$^{+2}$ and C$^{+1}$ are undecidable). These peaks, due to the almost equal m/z, are difficult to clearly define. M, z – mass and charge of the ion.

The powder 1 and its compact contain a significant amount of carbon (possibly magnesium). Powder 2 and compact 2 also contain a significant amount of carbon (possibly magnesium) and copper, which is absent in the powder 1 and compact 1. These elements are not considered further because their presence in detected quantities does not influence the homogeneity of the microstructure.

Iron and silicon can be possible sources of inhomogeneity of the structure during the sintering (not distinguished in mass-spectrometer), the total number of which is in many times higher than in powder 2 and compact 2. Titanium can also be the source of inhomogeneity, which is absent in powder 2.
Titanium was found only in powder 1, moreover its presence has random nature, i.e. it appears not in all measurements (Figure 3).

### Table 1 Composition of impurities in the powders and compacts obtained therefrom.

| Sample  | Fe, ppm | Cu, ppm | Ti, ppm | Mg, ppm | C, ppm | Cr, ppm | V, ppm | F, ppm | Se, ppm | Sum, ppm |
|---------|---------|---------|---------|---------|--------|---------|--------|--------|---------|----------|
| Powder 1 | >10 | >10 | >10 | >10 | 5800 |
| Compact 1 | >10 | <10 | >10 | >10 | 4100 |
| Powder 2 | 760(Si) | 630 | <10 | 720(C) | 720(Mg) | 60 | 50 | 20 | 50 | 2300 |
| Compact 2 | 740(Si) | 6700 | <10 | >10 | 120(Mg) | 7600 |

Figure 3. Fragments of mass spectrum for four independent measurements of both powders and their compacts. The multiplicity of the peaks for titanium for sample “Powder 1” is caused by the presence of five stable isotopes in its structure.

Thus, it was found out:

- In compact 1, in contrast to compact 2, the areas with bimodal structure having increased micro hardness are formed in the volume of compact.
- In the powder 1 and compact 1 the content of iron (silicon) is in several times higher than their content in the powder 2 and compact 2.
- In individual measurements for powder 1 the presence of titanium in its structure was revealed, which is absent in other measurements of the same sample, titanium is absent in the compact obtained from this powder. In the compact from powder 2 the presence of titanium was not found.

These findings suggest the existence between them of the casual relationships. Let’s start from the titanium.

3.1. The correlation between the doped titanium and bimodal structures

The random nature of the presence of titanium powder in powder 1 and its absence in compact indicates the presence in compact structure of relatively rare inclusions containing titanium. If the
micro-object in the impact zone of the laser beam, titanium is present in the mass spectrum. In the process of SPS the inclusion dissolves in the surrounding material, the titanium concentration falls below the detection limit (10 ppm). REM confirms the presence of foreign formations in compact 1 in the form of relatively large 10-2 microns) hollow spheres (Figure 4). Such objects are absent in compacts 2. Similar object in the nanopowder of aluminum oxide, obtained by blasting from metallic aluminum, are noted in operation. [8]

Figure 4. More examples of spherical objects in the compacts of powder 1 after free sintering in the dilatometer. Heating to 1460°C without holding (left), heating to 1380°C without holding.

The presence of micro analyzer in REM allowed to confirm the presence of increased content of titanium in this objects.

However, the addition of titanium oxide nanopowder into the powder 2, in the amount close in weight to sphere-like structures in powder 1 and compacts 1, didn’t have a significant effect on the microstructure of obtained by the SPS method from this mixture compacts 2. These studies exclude the role of the titanium impurity in the powder 1 in formation of bimodal areas with increased micro hardness.

3.2. The correlation between the impurities of iron and silicon and bimodal structures
According to the Table 1, powder 1 in comparison to powder 2 has a multiple excess of iron and silicon, as used mass-spectrometric method gives only rough estimates of concentrations of impurities. The influence of these elements on the microstructure of compacts 2 was studied separately through the adding of them of their oxides to the powder 2 and subsequent sintering of the resulting mixtures. Determining the value of additives, the studies were based on data from mass-spectrometer, shown in Table 1.

Mixing of carbonyl iron powder into powder 2 and consequent SPS of the mixture didn’t influence the structure of the compact. In contrast, the addition of silicon oxide into the nanopowder 2 after the sintering resulted in a formation of structure, similar to the bimodal with increase micro hardness, but with smaller size of large grains, uniformly distributed over the entire volume of the compact (Figure 5). This experiment confirms the special role of silicon oxide.

In the powder 1 the impurity is present initially. The fact that bimodal during the sintering bimodal areas have local nature can be caused due to an inhomogeneous distribution of silicon oxide in the powder, for example its agglomeration. The anomalous areas a formed where there is a cluster of silicon oxides agglomerates.
To test this hypothesis, powder 1 was subjected to the intense ultrasonic dispersion in alcohol, followed by drying in the air with continuous stirring. Though the bimodal structures changed the configuration, but were evenly distributed throughout the sample. This confirms the presence of the impurity of silicon oxide in the powder 1 in the agglomerated state.

4. Conclusions
The study showed a significant effect of technological impurities in nanopowders on the microstructure of the materials obtained in spark-plasma sintering.

Considering the identified technological impurities, the greatest influence on the formation of microstructure during SPS showed an impurity of silicon, as a natural contaminant present in the powder 1.

Acknowledgements
This work was performed within the framework of the Center of Nuclear Systems and Materials supported by MEPhi Academic Excellence Project (contract № 02.а03.21.0005, 27.08.2013).

References
[1] Kisliy P S, Gevorkyan E S, Shkuropatenko V A and Gutsalenko Y G 2010 Superhard materials 68 24
[2] Rodriguez-Suarez T, Dhaz L A, Torrecillas R and others 2009 Sci. and Technol. 69 2467–73
[3] DongTao, Jiang W Z, Dustin M, Hulbert Z, Umberto Anselmi-Tamburini et al. 2008 The American Ceramic Soc. 91 151
[4] Wang S W, Chen L D, Hirai T 2000 Mat. Res. Soc. 15 (4) 982
[5] Dyatlova Y G, Ploshchanskiy Y S, Boikov S Y and others 2011 Proc. of the int. conf. on nanomaterials
[6] Samokhin A V, Alekseev N V, Tsvetkov Y V 2006 High energy chemistry 40 (2) 120
[7] Sirotinkin V P, Shamrai V F, Samokhina A V and others 2012 Inorganic materials 48 (4) 409
[8] Bukaemsky A A, Beloshapko A G and Puzyr A P 2000 Physics of combustions and explosions 36 (5) 119