

## Nanocomposites TiN – TiB<sub>2</sub>, TiN – Si<sub>3</sub>N<sub>4</sub> Consolidated by Electric Discharge Technology

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Investigation of consolidation process by electric discharge sintering (EDS) at the temperatures 1400 – 1550 °C for nanostructured high melting point powders and composition are described in the paper. In the present work we apply EDS technology to consolidate nanocomposites in the system TiN – TiB<sub>2</sub>, TiN – Si<sub>3</sub>N<sub>4</sub>. Influence of green body form and conductivity of the nanopowders on the densification process and mechanical properties of sintered bodies are studied. Sintering experiments were carried out in CO atmosphere

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### 1. INTRODUCTION

Commonly, electric discharge sintering (as called Spark Plasma Sintering) recognized by the most investigators as a field assisted sintering technique (FAST) which gives the possibility to consolidate the necessary materials in the shortest time. Short time of the process makes EDS attractive to consolidate nanopowders of various metals and ceramics and obtain nanostructured materials [1-4]. The other advantages of the method are fast process time, pressure up to 200 MPa, and possibility to use gases or vacuum as protected medium. Ceramic composites based on boron carbide, titanium nitride and boride demonstrate high industry required properties and parts consolidated from the components widely used as cutting tools, crucibles, parts of mechanisms etc. In our investigation we consolidate nanocomposites in the system TiN – TiB<sub>2</sub>, TiN – Si<sub>3</sub>N<sub>4</sub> applying EDS technology to obtain dense ceramics in the form factor of cylinder, ball or ring and test its mechanical properties.

### 2. EXPERIMENTAL METHODS

The objects of our investigations are nanopowders mixtures TiN – TiB<sub>2</sub>, TiN – Si<sub>3</sub>N<sub>4</sub>. Nanopowders of TiN,

Si<sub>3</sub>N<sub>4</sub> and TiN – TiB<sub>2</sub> were synthesized plasmachemically and purchased from PCT ltd. (Latvia).

The EDS experiments for consolidation of composite powders mixtures have been carried out using an «ERAN-2/1» equipment designed in IPMS NASU. Parameters like direct current, temperature, bottom piston travel were monitored during the experiment. Data about shrinkage of nanopowders during EDS consolidation process were monitored as travel of bottom piston (the upper piston is fixed) and recalculated in corresponded densities of specimens. Around 1 – 1,5 g of the nanopowder or nanocompositions were loaded in a graphite die 10 mm diameter with punch unit and applying pressure ~ 70 MPa (300 kg) to establish good contacts as between particles as graphite instruments – powder. The sintering experiments were organized by the next parameters: direct current strength – up to 1,1 kA, alternative current with increased frequency (5,1 kHz) 0,3 kA, duration of sintering 120 – 300 sec. Under this condition the temperatures 1400 – 1650 °C have been achieved.

Characterization of the powders used in the work is presented in the Table 1.

Table 1 – Nanopowders and nanocompositions characterization

Powder/composition	Specific surface, m <sup>2</sup> /g	[N], %	Average particle size, nm
TiN – 20wt %TiB <sub>2</sub>	54	0.8	60 (grain)
TiN – 50wt %TiB <sub>2</sub>	–	–	80 (grain), 180 (agglomerate)
TiN – 40wt %Si <sub>3</sub> N <sub>4</sub>	122 <sub>+10</sub>	27,9 ± 0,3	30 (grain), 200(agglomerate)

### 3. CHARACTERIZATION

The densities of the EDS consolidated materials were measured by the Archimedes method in deionised water at room temperature. Additionally, particle size of nanopowders was estimated by light scattering and photon correlation measurements on “Zetasizer 1000 HS”. The Vickers hardness, fracture toughness of sintered composite ceramics were measured under load 2 kg (Micromet 2103), nanohardness were measured

under load 20 g (Micron-gamma). The microstructure of sintered composites was observed by Jeol Superprobe 733 scanning electron microscopy (SEM).

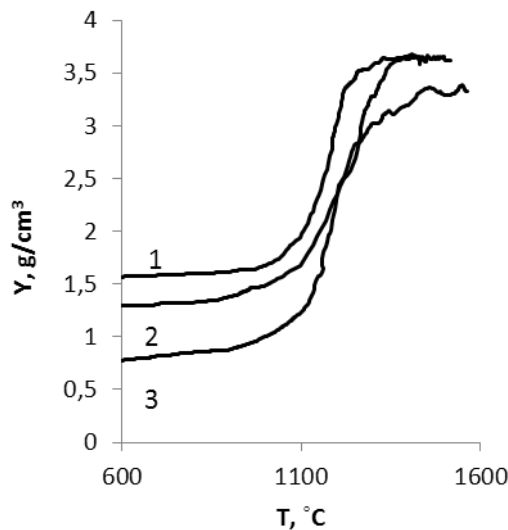
### 4. RESULTS AND DISCUSSION

#### 4.1 Densification of Si<sub>3</sub>N<sub>4</sub> – TiN, nanopowders

Densification of Si<sub>3</sub>N<sub>4</sub> – TiN, nanopowders presented on the Fig. 1. The samples were sintered in the form

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of sphere, ring and cylinder. Green density of  $\text{Si}_3\text{N}_4$ –TiN composition in form of sphere and cylinder were estimated as 35–40 %, but material in form ring has 20 % initial density. Compare the results of EDS consolidated  $\text{Si}_3\text{N}_4$ –TiN nanopowders in the form of cylinder, ring and sphere (see fig.1) may be noticed what shrinkage of all samples starts at the temperature  $\sim 1100$  °C Specimen in the form of cylinder density more actively up to the temperature in 1400 °C. Densification process of ring and sphere finished at the relatively higher temperature in 1500 °C, because of bigger volume of the material and inhomogeneous temperature field connected with complex form of die and punches. For these materials additional investigation is invited to select sintering regime which permit to heat powder volume homogeneously.



**Fig. 1** – Densification curves of TiN – 40wt % $\text{Si}_3\text{N}_4$  nanopowders 1 – cylinder, 2 – sphere, 3 – ring

Generally, the consolidation process of  $\text{Si}_3\text{N}_4$ –TiN composition did not exceeding 250 s.

Common view of EDS consolidated samples presented on the Fig. 2.

#### 4.2 Microstructure and properties

SEM micrographs of TiN –  $\text{TiB}_2$  and  $\text{Si}_3\text{N}_4$ –TiN EDS consolidated samples are shown in Fig. 3. Estimated grain size of TiN –  $\text{TiB}_2$  composite is 250–350 nm, the grain size of  $\text{Si}_3\text{N}_4$ –TiN composite is 250–300 nm. At the

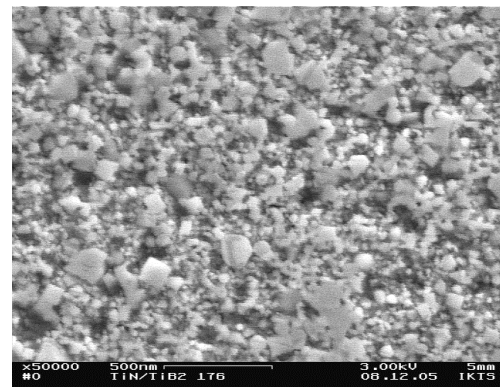
**Table 2** – Mechanical properties of EDS consolidated nanocompositions

Composition	Form of sample	Properties		
		Nano-hardness, GPa	HV, GPa	$K_{1c}$ , $\text{MPa m}^{1/2}$
TiN – 40wt % $\text{Si}_3\text{N}_4$	cylinder	$28,67 \pm 8,6$	$17,8 \pm 0,6$	6,3
	ball	$26,58 \pm 4,7$	$16 \pm 1$	4,99
	ring	–	$13,9 \pm 1,2$	–
TiN 50wt % $\text{TiB}_2$	cylin-der	$39,47 \pm 1,4$	$17 \pm 1,9$	4,5
TiN 20wt % $\text{TiB}_2$	cylin-der	–	$21,6 \pm 2,7$	–

same time round shape grains with average grain size  $\sim 3$ – $8$   $\mu\text{m}$  were observed. These grains could be addressed to TiN abnormal sinterability in agglomerates during EDS process [3].



**Fig. 2** – Samples of EDS consolidated  $\text{Si}_3\text{N}_4$ –TiN, TiN –  $\text{TiB}_2$  compositions



**Fig. 3** – Scanning electron microscope micrograph of nanostructured powder after consolidation TiN – 20wt % $\text{TiB}_2$

Mechanical properties of consolidated materials are the function of their final microstructure. Mechanical properties (Vickers hardness at  $P = 100$  g, nanohardness at  $P = 20$  g and fracture toughness at  $P = 2000$  g) for EDS consolidated materials presented in the Table 2. For the compositions TiN – 40wt % $\text{Si}_3\text{N}_4$  mechanical properties were measured for sintered bodies in the form of sphere, ring and cylinder, and the rest of the samples were measured in the form of cylinder.

The highest nanohardness  $28,67 \pm 8,6$  GPa and fracture toughness  $6.3 \text{ MPa m}^{1/2}$  demonstrate sample in form of cylinder. It's explained by fine and homogeneous structure of the composite. The other samples in the form of ring and ball need higher temperatures to obtain dense material and finally we obtain coarse grain composites.

As expected, for the composition TiN – TiB<sub>2</sub> the highest nanohardness was measured for material TiN – 50wt %TiB<sub>2</sub> ~ 39 GPa. Sample with 20wt %TiB<sub>2</sub> didn't test on nanohardness because of relatively high open porosity. Measured Vickers hardness of the TiN – 20wt %TiB<sub>2</sub> nanocomposite is relatively higher than TiN – 50wt %TiB<sub>2</sub>. But, hardness data distribution for the sample with 20wt %TiB<sub>2</sub> denotes on inhomogeneous distribution of TiB<sub>2</sub> phase in the volume of composition and needs in additional investigation.

## 5. CONCLUSIONS

Implementation of the electric discharge sintering technique is potentially interesting to fabricate dense

nanocrystalline materials and decrease the process time and temperature compared with traditional pressureless sintering or hot pressing. The possibilities of the EDS method to consolidate materials in a different form (balls, rings, cylinders) are investigated. Nanocomposites Si<sub>3</sub>N<sub>4</sub> – TiN could be successfully EDS consolidate at the temperature ~ 1500 °C to bulk material with average grains size ~ 300 nm. The effect of TiN aggregation during EDS treatment in the big grains ~ 3 – 5 μm is observed. The highest nanohardness  $28,67 \pm 8,6$  GPa and fracture toughness  $6.3 \text{ MPa m}^{1/2}$  demonstrate sample Si<sub>3</sub>N<sub>4</sub> – TiN in form of cylinder.

The composite TiN – TiB<sub>2</sub>, has been successfully consolidated at relatively low temperatures 1400 – 1450°C to the dense nanocomposites with nanohardness ~ 39 GPa for material TiN – 50wt %TiB<sub>2</sub>.

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