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Nanocomposites TiN – TiB_2, TiN – Si_3N_4 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_2, TiN – Si_3N_4. 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

Keywords: Nanocomposites; Electric discharge-sintering, TiN, Si_3N_4, TiB_2.

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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_2, TiN – Si_3N_4 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_2, TiN – Si_3N_4. Nanopowders of TiN, Si_3N_4 and TiN – TiB_2 were synthesized plasmacemically 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^2/g	[N], %	Average particle size, nm
TiN – 20wt %TiB_2	54	0.8	60 (grain)
TiN – 50wt %TiB_2	–	–	80 (grain), 180 (agglomerate)
TiN – 40wt %Si_3N_4	122±10	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), nanohardnes 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_3N_4 – TiN, nanopowders

Densification of Si_3N_4 – TiN, nanopowders presented on the Fig. 1. The simples were sintered in the form

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of sphere, ring and cylinder. Green density of Si_3N_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 Si_3N_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 ~ 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.

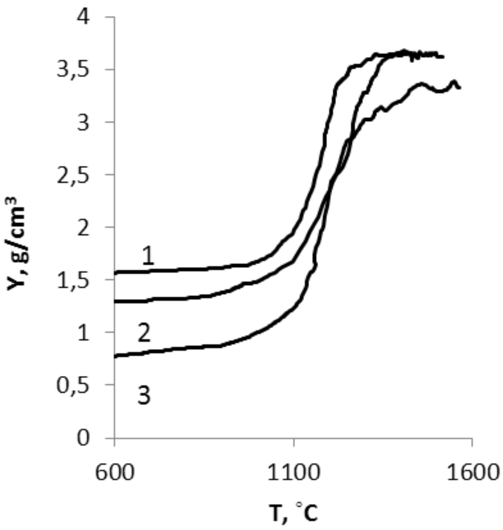

Fig. 1 – Densification curves of TiN – 40wt %Si_3N_4 nanopowders 1 – cylinder, 2 – sphere, 3 – ring

Generally, the consolidation process of Si_3N_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 – TiB_2 and Si_3N_4 – TiN EDS consolidated samples are shown in Fig. 3. Estimated grain size of TiN – TiB_2 composite is 250 – 350 nm, the grain size of Si_3N_4 – TiN composite is 250 – 300 nm. At the same time round shape grains with average grain size ~ 3-8 μm were observed. These grains could be addressed to TiN abnormal sinterability in agglomerates during EDS process [3].

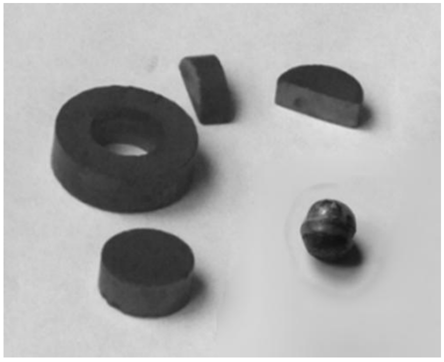

Fig. 2 – Samples of EDS consolidated Si_3N_4 – TiN, TiN – TiB_2 compositions

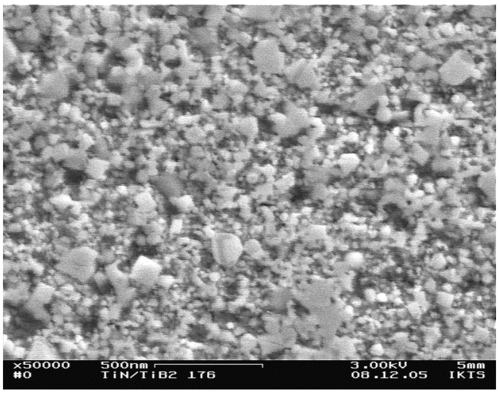

Fig. 3 – Scanning electron microscope micrograph of nanostructured powder after consolidation TiN – 20wt %TiB_2

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 %Si_3N_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.

Table 2 – Mechanical properties of EDS consolidated nanocompositions

Composition	Form of sample	Properties		
		Nano-hardness, GPa	HV, GPa	K_{1C}, MPa·m$^{1/2}$
TiN – 40wt %Si_3N_4	cylinder	28,67 ± 8,6	17,8 ± 0,6	6,3
	ball	26,58 ± 4,7	16 ± 1	4,99
	ring	–	13,9 ± 1,2	–
TiN 50wt %TiB_2	cylin-der	39,47 ± 1,4	17 ± 1,9	4,5
TiN 20wt %TiB_2	cylin-der	–	21,6 ± 2,7	–

The highest nanohardness 28,67 ± 8,6 GPa and fracture toughness 6.3 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_2 the highest nanohardness was measured for material TiN – 50wt %TiB_2 ~ 39 GPa. Sample with 20wt %TiB_2 didn't test on nanohardness because of relatively high open porosity. Measured Vickers hardness of the TiN – 20wt %TiB_2 nanocomposite is relatively higher then TiN – 50wt %TiB_2. But, hardness data distribution for the sample the with 20wt %TiB_2 denotes on inhomogeneous distribution of TiB_2 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 preasureless sintering or hot pressing. The possibilities of the EDS method to consolidate materials in a different form (balls, rings, cylinders) are investigated. Nanocomposites Si_3N_4 – 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 ± 8,6 GPa and fracture toughness 6.3 MPa·m^{½} demonstrate sample Si_3N_4 – TiN in form of cylinder.

The composite TiN – TiB_2, has been successfully consolidated at relatively low temperatures 1400 – 1450°C to the dense nanocomposites with nanohardness ~ 39 GPa for material TiN – 50wt %TiB_2.

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