Preparation of SiC–$MgAl_2O_4$–$Y_3Al_5O_{12}$-MWCNTs nanocomposites by spark plasma sintering

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Abstract. Fabrication a composite materials based on silicon carbide (SiC) reinforced with multi-walled carbon nanotubes (MWCNTs) with addition of magnesium alumina spinel $MgAl_2O_4$, and yttrium aluminum garnet $Y_3Al_5O_{12}$ by spark plasma sintering are presented.

Two series of composites differing by the particle size of starting SiC were prepared. Mechanical characteristics of composites including microhardness, fracture toughness and flexural strength are determined.

1. Introduction

In recent years, in aerospace engineering there is a trend for the use of ceramic composite materials at sites exposed to high temperatures (1500 K) and aggressive environment. This is because, ceramics and composite materials in these conditions have higher characteristics compared to metals and alloys, particularly flexural strength [1]. However, ceramics is a more brittle material, therefore, the most promising are materials combining strength and thermal stability of ceramics and a sufficiently high fracture toughness and elasticity [2, 3].

Silicon carbide is one of the most promising oxygen-free refractory compounds for obtaining construction materials for use at high temperatures. Reinforcement of ceramics with various additives (powders, fibers, nanotubes) leads to a significant increase in strength and fracture toughness, which place the ceramic composite materials on one of the first places among the promising structural materials for aerospace engineering [4, 5, 6].SiC-based composites are also promising for use as protective armor [7]. Popular sintering additives for silicon carbide ceramics are oxides (such as Al_2O_3, Y_20_3, RE_2O_3, MgO, etc.) and their mixtures that create a liquid-phase sintering of SiC composites providing the notable lowering of synthesis temperature. It was found that oxide additives facilitate densification of sinters and significantly improve mechanical properties of SiC ceramics [8, 9]. The microstructure of such materials is characterized by a framework of crystalline grains surrounded by a layer of inter-granular phases [10, 11].

Among common reinforcing constituents, the most preferred care are the carbon nanotubes demonstrating excellent mechanical properties that can improve the performance of a polycrystalline ceramic matrix, such as hardness, strength, Young's modulus , fracture toughness, wear resistance [12, 13].

There are many routes for the fabrication of silicon carbide. Spark Plasma Sintering (SPS) stands out among them. It is a recent development in sintering technology that combines axial pressure with

heating by an electrical current passing through the die that contains the powder body. The basic idea of SPS is to heat a powder material by passing a pulsed current with simultaneous pressure application [14]. It provides very fast heating and lower sintering temperatures allowing preparation of materials with a high compactness in a few minutes [15].

The important advantage of this process is the possibility to obtain dense material with a fine microstructure due to the very low sintering time at low temperature. There are some reports on the SPS synthesis of SiC composites containing separately either oxide additives [16, 17] or multi-walled carbon nanotubes [18, 19]. It is possible that simultaneous introduction of two different reinforcing agents as oxide dopants and MWCNTs could give a synergetic effect in improvement of mechanical properties.

In this report we present the results on fabrication of SiC nanocomposites containing together the multi-walled carbon nanotubes and complex oxides if form of magnesium alumina spinel $MgAl_2O_4$, and yttrium alumina garnet $Y_3Al_5O_{12}$ by the Spark Plasma Sintering.

2. Experimental

As the starting materials the commercially available industrial products, namely SiC powder and multi-walled carbon nanotubes were used. We used two different batches of silicon carbide: first one with an average size of 2-3 μm, and second one with the particle size up to 30 microns. Based on these batches two corresponding series of composites were fabricated (series #1 from batch #1 and series #2 from batch #2). Both kinds of SiC powders were subjected to additional treatment in hydrofluoric acid HF for removing residual SiO_2 impurity.

The additives of magnesium alumina spinel $MgAl_2O_4$, and yttrium alumina garnet $Y_3Al_5O_{12}$ were prepared in nanodisperse form by specific version of sol–gel technology [20, 21], the fundamental essence of which is to obtain a gel of high molecular weight polymer and realize the distribution in it the homogenous true solution of several oxide components derived from the nitrates and chlorides of the metals. The dried xerogel is calcined at relatively low temperatures (from 600 to 1100^{o}C depending on the type and nature of the oxide), turning the porous mass into granular agglomerated powder consisting of flakes with a size of 50-70 microns that in turn are consisting of nanoparticles of the resulting oxide.

Commercial multi-walled carbon nanotubes produced by Bayer Material Science AG were used as main reinforcing component for SiC-based composites. The outer diameter and inner diameter of the MWCNT are around 13 nm and 4 nm respectively and MWCNT length is less than 1 micron. The bulk density of nanotubes was 0.13-0.15 g/cm^3. The nature as well as the way of special treatment of carbon nanotubes strongly influence on the structure and strength of ceramic composites [22]. MWCNTs have previously been calcined at 300^{o}C for removing a preservative agent. Further the nanotubes were subjected to sonication in polyvinyl alcohol solution. The use of ultrasound allows dispersing MWCNTs in a liquid by the destruction of their agglomerates, particularly the large bundles and aggregates.

In the course of development we tried different surfactants as the dispersion medium, including methyl, ethyl, isopropyl alcohol solutions and water. This has been studied in detail in work [23]. The comparative study of destruction efficiency and stability of solution shoved that polyvinyl alcohol (PVA) is the most suitable dispersion surfactant. We have developed a method of CNTs dispersing in PVA solution (concentration 0.1%). Dispersion of MWCNT performed using ultrasound dispersant Sonoplus HD 3100, with power 100 W, dispersing time 10-20 minutes, frequency of 22 kHz, the pulse duration 1-1.5 seconds and duty cycle of 1 sec. As a result we obtained the homogenized suspension, stable up to 48 hours.

After the dispersion, the suspension containing MWCNTs was mixed with SiC powder. The mixing of all the components of the composite material was performed using a planetary mill for 20–40 min. Then, after separation of the suspension from the grinding media, it was placed in a heat resistant bowl and exposed to the drying. After a series of investigations it was found that the best results of drying are obtained by simultaneous heating from bottom (using an electric hotplate) and from top (using an

infrared lamp) under constant stirring. In this case, it is used a low-temperature drying from IR lamp source. The distance between the lamp and the surface of the heated object is 5 - 12 cm. This simultaneous deep and surface heating from two sources under continuous stirring results in a quick drying of the slurry; no peeling MWNTs or sedimentation of individual particles occurs during the procedure. Thus it is achieved a uniform distribution of all components of the ceramic composite material. The resulting powder was further homogenized by rubbing through a sieve with a mesh size of 0.25 mm to increase the homogeneity, flowability and ease filling of the mold by press-powder.

The composite samples were prepared by spark plasma sintering on installation 25 D HP (FCT Systeme, Germany) at a temperature in the range of 2000-2200 °C with heating rate 450 ^{o}C/min under pressure 19-22 kN and exposure at maximal temperature 10-15 minutes. Resulting composite samples appeared as dark gray discs of 20 mm in diameter and 4.5 mm thick. Polishing of material carried on grinding and polishing machine EcoMet 250 (Buehler, Germany).

The measurements of the composite micro-hardness were performed on apparatus Micromet 5114 by Vickers pyramid indentation. Determination of the average micro-hardness of the sample was performed at loads in the range of 200-300 g., the loading time for all tests was 15 seconds (5 seconds-load, 10 seconds – exposure under load). 5 prints were done on the each sample.

The micro-hardness indentation method was using also to measure fracture toughness (K_{1C}). For calculation used the following relation [24]:

$$K_{1C} = 0{,}016\ (E/H)^{1/2}\ (P/c^{3/2}), \quad (1)$$

where *E* and *H* are Young's modulus and hardness, respectively, P is the applied load, *c* is the radial crack length. The load on the indenter in the measurements was 19.6 N.

Investigation of the thermo-mechanical properties of the samples was performed on a high-temperature electromechanical universal machine UTS 110M with a nominal load of 100kN and furnace VE-324-RM. A study of the thermo-mechanical properties of SiC-based composites was carried out by three-point bending at a temperature of 1500 °C under vacuum (10^{-2}Torr). The heating rate was 10 °C per minute. Calculation of flexural strength was performed according to relation:

$$\sigma = \frac{3 \cdot P \cdot l}{2 \cdot b \cdot h^2}\ \text{(MPa)}, \quad (2)$$

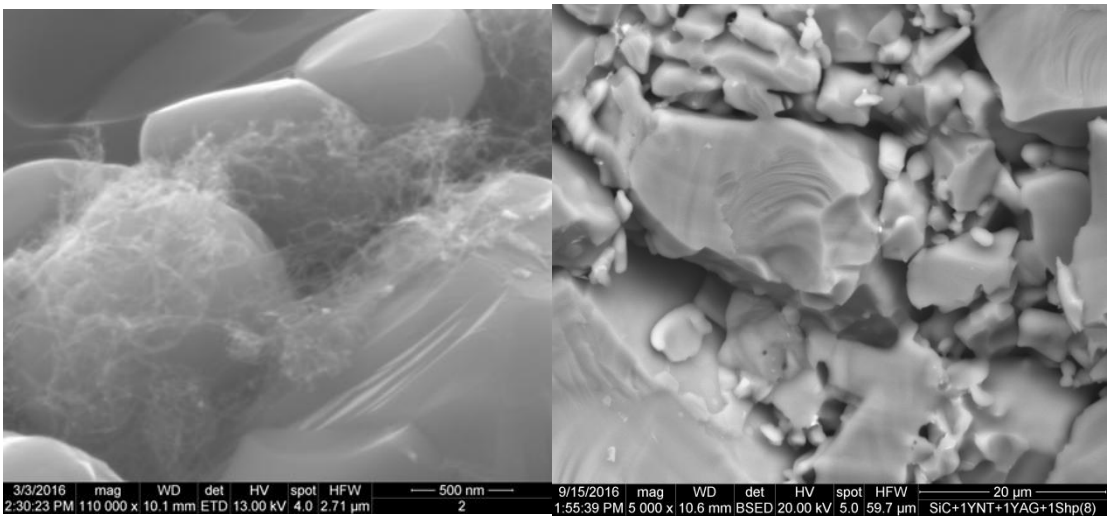
where *P* - breaking load in N, *l* - span in mm, *b* - width of the specimen in mm,
h - the thickness of the sample in mm.

3. Results and Discussion

The microstructure of samples belonging to series #1 is formed from dense equi-crystallite material with grain size a few microns. Nanotubes are distributed rather uniformly over the entire volume. The nanotubes form in the SiC ceramic composite a reticular framework along the facets of the crystals of the ceramic matrix, like it is in alumina-CNT composites [25], that impedes the growth of SiC grains and promotes the removal of the closed porosity. These reticular carcasses strongly contribute to the increase in the mechanical properties of composite. The microstructure of SiC + 6% MWCNTs + 1% $MgAl_2O_4$ composite shown on Fig. 1a presents rather uniform distribution of silicon carbide crystals with size 2-3 microns that covered by reticular-carcass framework of carbon nanotubes. As can be seen from Table 1, such representative mechanical properties as micro-hardness and fracture toughness are increasing after addition of magnesium alumina spinel and then yttrium alumina garnet.

It is believed [26] that oxides, like YAG, spinel, Al_2O_3 and some others, either due to reaction with passivating silica layer coating the SiC grains, or due to reaction among themselves, form liquid phases during sintering. On one hand they activate the densification processes, and on the other they improve some material's properties. We assume that appearance of fine films formed by magnesium alumina spinel and YAG around grains of silicon carbide provides the slowing down migration of their boundaries, and together with MWCNTs inhibits the SiC grain growth. Moreover, due to the

chemical interaction between $MgAl_2O_4$ and $Y_3Al_5O_{12}$ and formation of eutectics, as well as due to the difference of the melting points (2135°C for spinel and 1950°C for YAG) their joint action takes place in a broader temperature range that contributes to a more fine-grained and homogeneous structure.



(a) **(b)**

Figure 1. SEM image of a cleaved samples:SiC + 6% MWCNTs + 1% $MgAl_2O_4$ (series #1) **(a)** SiC + 1% MWCNTs + 1% $MgAl_2O_4$ + 1% $Y_3Al_5O_{12}$ (series #2) **(b)**

The following to spinel addition of yttrium-aluminum garnet leads to further suppression of growth of silicon carbide crystals in the composite during sintering. The reduction in the grain size of SiC-MWCNTs ceramic matrix composite containing both additives $MgAl_2O_4$ and $Y_3Al_5O_{12}$ is notable compared to single doping by spinel. The grain size of SiC becomes only 0.5-2 microns. This behavior results in further enhancement of mechanical properties of composite including high-temperature characteristics (see Tables 1 and 2).

Table 1. Averaged values of the mechanical properties of the samples of series #1

Composite	**Load (g)**	**Microhardness (GPa)**	**Fracturetoughness (MPa/m^2)**
SiC+6%MWCNT	300	28,3	4,3
SiC+6%MWCNT +1% $MgAl_2O_4$	300	31,4	5,1
SiC+6%MWCNT +1% $MgAl_2O_4$ +1% $Y_3Al_5O_{12}$	300	34,8	5,7

Note: The contents of MWCNT and oxide additives here and below are given in vol. %.

Composites of series #2 demonstrate the double-fractional grain structure shown on Fig.1b. Large difference in size of crystals and presence of small grain fraction results in the better densification of structure due to the distribution of fine grains of silicon carbide around the majorones. Nevertheless such dense packing doesn't result in full-dense structure and demonstrate the presence of certain amount of closed pores, as it can see from Fig.5. However, this structure and the presence of large crystals surrounded by small grains, leads to uneven and hindered cracks propagation. Fracture toughness measured by the method of indentation of Vickers pyramid corroborates that (see Table 3).

Table 2. The thermo-mechanical properties of composites of series #1

Composite	Load (g)	Microhardness (GPa)	Fracturetoughness (MPa/m^2)
SiC+6%MWCNT	300	28,3	4,3
SiC+6%MWCNT +1% $MgAl_2O_4$	300	31,4	5,1
SiC+6%MWCNT +1% $MgAl_2O_4$ +1% $Y_3Al_5O_{12}$	300	34,8	5,7

Table 3. The mechanical and thermo-mechanical properties of composites of series #2

Composite	Microhardness (GPa)	Fracturetoughness (MPa/m^2)	Flexural strength at 25^{o}C, (MPa)	Flexural strength at 1500^{o}C (MPa)
SiC	32,8	3,77	240	130
SiC+1% MWCNT	31,3	4,05	280	160
SiC+6% MWCNT +1% $Y_3Al_5O_{12}$	33,3	5,62	270	170
SiC+1% MWCNT +1% $Y_3Al_5O_{12}$	33,7	8,01	320	210
SiC+1% MWCNT+1% $MgAl_2O_4$	32,7	5,69	310	200
SiC+1% MWCNT +1% $Y_3Al_5O_{12}$ +1% $MgAl_2O_4$	32,2	8,67	390	280

Comparison of data presented in Tables 1-3 shows that other mechanical properties, such as micro-hardness and flexural strength of composites of series #1 and #2 are rather close to each other. Only difference is in fracture toughness, which reaches to 8 MPa/m^2 in case of composites belonging to series #2. We believe that increased value of fracture toughness caused by double-fractional grain structure of the composites. The influence of YAG and spinel addition on mechanical properties of series #2 composites is similar to that for series #1.

4. Conclusions

The composite materials based on silicon carbide reinforced with multi-walled carbon nanotubes with addition of magnesium alumina spinel $MgAl_2O_4$, and yttrium aluminum garnet $Y_3Al_5O_{12}$ fabricated by spark plasma sintering. As starting materials two different SiC commercial powders with particle sizes 2-3 μm and up to 30 μm used for composites fabrication.

The commercial multi-walled carbon nanotubes produced by Bayer MaterialScience AG, and the nanodisperse additives $MgAl_2O_4$and $Y_3Al_5O_{12}$ prepared by specific version of sol–gel technology were used as additives.

Introduction MWCNT increases the mechanical properties (strength and crack resistance) of composite material compared to silicon carbide ceramics.

Additives $MgAl_2O_4$ and $Y_3Al_5O_{12}$not only increase the strength characteristics of the material, but also lead to the suppression of SiC crystal growth during sintering, resulting in increased strength and reduced porosity of the composite.

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