DC conductivity of silicon nitride based carbon-ceramic composites

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Abstract

The silicon nitride ceramics are usually known as strongly refractory and enduring materials and have typical electrically insulating properties. If the reinforcing phase of ceramic composite (that is mainly put in the material to improve mechanical properties) is a good electrical conductor, it is worth to investigate the composite in electrical aspect. In this work carbon nanotubes, black-carbon and graphite were added to the basic silicon nitride ceramic and the electrical conductivity of the prepared carbon-ceramic composites was determined. The conductivity of the ceramic composites with different type and concentration of the carbon additives was observed by applying four point DC resistance measurements. Insulator and conductor composites in a wide conductivity range can be produced depending on the type and quantity of the additives. The additive types as well as the sintering parameters have influence on the basic electrical properties of the conductor composites.

Keywords: silicon nitride, carbon nanotube, DC conductivity, percolation conduction

I. Introduction

From electrical point of view ceramic materials are usually applied typically as insulator products. During our research a Si_3N_4 ceramic with extreme mechanical and thermal properties was developed [1–3], but from electrical point of view it was an insulator. Our aim was to develop a hi-tech ceramic that has excellent electrically conductive property as well. To reach this, small amount of electrically conductive additives were mixed into insulator silicon nitride ceramic. Carbon nanotubes (CNT) are the most popular reinforcing material in building composite structures because they show advantageous mechanical, electrical and thermal properties [4–7]. Therefore, the application of CNTs was the main line of building up of the ceramic composites. In case of appropriate mixing of CNTs the fibrillated second phase interlaces the material, so the electrical current can flow through it freely in a percolative way. For comparison, the effect of other carbon additives was also examined. To ensure the appropriate structure two types of sintering method were tried out. Furthermore, a matrix base material that contains electrically conductive part (aluminum nitride) was applied to improve electrical conductivity. Carbon-ceramic composites with electrical conductivity in a wide range have been successfully produced.

II. Experimental Procedure

Composition of the starting powder mixture of silicon-nitride base material can be seen in Table 1. Two types of basic ceramics were used. The first one, signed by A, was prepared from α-Si_3N_4 powder (Ube SN-ESP), whereas the second one, signed by B, was produced from mixture of the α-Si_3N_4 powder and 4 wt% of hexagonal single phase AlN powder (H.C. Starck GradeC). In addition, Al_2O_3 (Alcoa A16) and Y_2O_3 (H.C. Stack Grade C) powders were added as sintering additives.

The reinforcing second phase, CNT (d = 10–20 nm, l = 8–10 μm, Department of Applied and Environmental Chemistry of the University of Szeged), graphite (GR) (d = 1–2 μm, Aldrich Synthetic graphite powder) or black-carbon (BC) (d = 50–100 nm, Taurus N330), was

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added to the starting powder mixture in a ration 1–10 wt% (Table 1) to modified the electrical properties of the basic ceramic matrix. The composite powder mixtures were milled in a planetary type alumina ball mill in ethanol to obtain better homogeneity. Forming of green samples was performed with addition of organic bonding material (polyethylene-glycol, Hoechst Polyglycol 6000 S) by uni-axial dry pressing at 220 MPa. During experiments two types of sintering method were used (Table 1). In case of HIP (Hot Isostatic Pressing) sintering was done at 1700°C on 20 MPa in N_2 (purity 99.999%) atmosphere for 3 hours holding time. In case of GPS (Gas Pressure Sintering) method heat treatment was completed at 1700°C on 2 MPa [8]. The final size of the samples was 3.5×5×50 mm. After the sintering the surface and the edges of samples were polished down by diamond plate. During the structure examination Philips PW 1050 diffractometer was used to determine the phase compositions and LEO 1540 XB scanning electron microscope to study the morphology.

Table 1. Variation of sintered carbon-ceramic composites

Basic ceramic					Conductive phase			Sintering technique
Type	Si_3N_4 [wt%]	AlN [wt%]	Al_2O_3 [wt%]	Y_2O_3 [wt%]	GR [wt%]	BC [wt%]	CNT [wt%]	
A	90	–	4	6	–	–	–	GPS
B	87	4	4	5	–	–	–	GPS
A	90	–	4	6	–	–	–	HIP
B	87	4	4	5	–	–	–	HIP
A	90	–	4	6	1	–	–	GPS
A	90	–	4	6	1	–	–	HIP
A	90	–	4	6	–	1	–	GPS
A	90	–	4	6	–	1	–	HIP
A	90	–	4	6	–	–	1	GPS
B	87	4	4	5	–	–	1	GPS
A	90	–	4	6	–	–	1	HIP
A	90	–	4	6	–	–	3	GPS
A	90	–	4	6	–	–	3	HIP
A	90	–	4	6	5	–	–	GPS
A	90	–	4	6	5	–	–	HIP
A	90	–	4	6	–	5	–	GPS
A	90	–	4	6	–	5	–	HIP
A	90	–	4	6	–	–	5	GPS
B	87	4	4	5	–	–	5	GPS
A	90	–	4	6	–	–	5	HIP
B	87	4	4	5	–	–	5	HIP
A	90	–	4	6	10	–	–	GPS
A	90	–	4	6	10	–	–	HIP
A	90	–	4	6	–	10	–	GPS
A	90	–	4	6	–	10	–	HIP

To do the electrical measurements accomplishable electrical contacts (4 on each sample) were put on the surface of the samples. As a result of numerous probes a multilayer contact consisting of 4 layers was produced (Fig. 1a). Thin gold layer was vapoured on the appropriate part of surface of the sample. The gold layer was covered by conductive glue (Elektropol) that contains silver grains. After drying the current feeds were fixed on this layer by ordinary soldering technique. The created contacts have low resistance in order to not to prevent the overload of the measure-ment system.

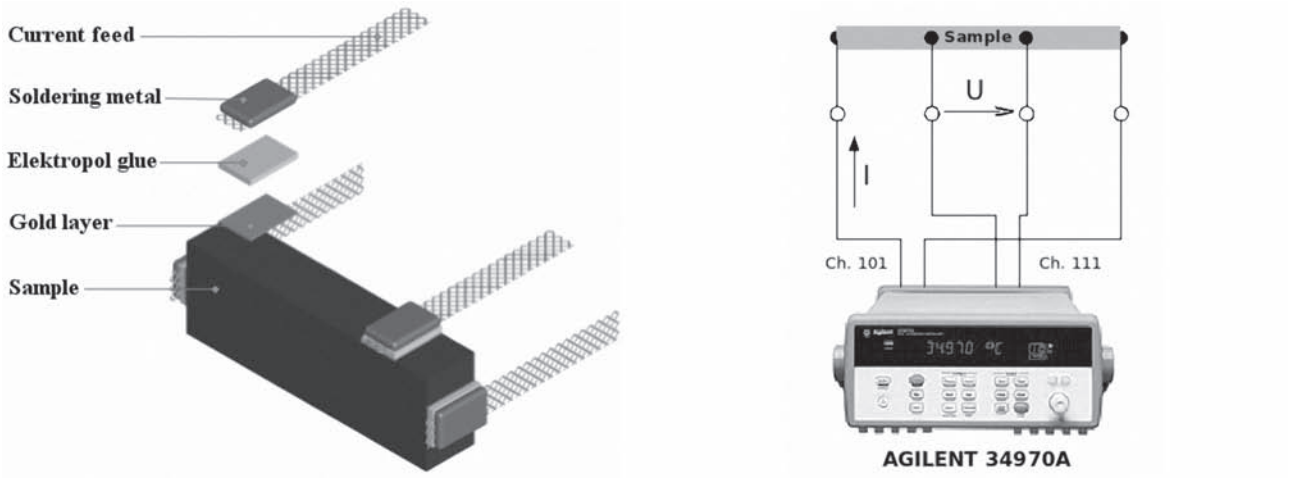
To determine electrical conductivity four point DC (direct current) resistance measurement was applied (Fig. 1b). During the measurement the sample was being excited through the two outside contacts by DC signal while the voltage between the two inner contacts was detected. For choosing the measurement range of the equipment resistance of the contacts has to be considered. This resistance was determined on the basis of a simply two points method. The specific conductivity of the sample was calculated on the basis of Ohm law [9].

III. Results and Discussion

The examined composites can be grouped into insulator and conductor types as resulted from four points DC resistance measurements. Samples that overloaded our measurement system (10 MΩ measurement limit) can be considered as insulator because their resistance was not measurable. These samples were: basic ceramics without any type of additives, samples that contains 1 wt% graphite, CNT, and BC samples with 5 and in some cases 10 wt% graphite.

The other group of composites is considered to be conductor because of the contact and grouping of the additives. As the electrical conduction takes place through the paths that are made by linked conductive phases these materials behave like percolative conductors. The percolation thresholds observed in composites are 3 wt% for CNT, 5 wt% for BC and 10 wt% for graphite. In Fig. 2 specific conductivity range of the composites according to type, concentrate of additives, sintering technique and type of matrix ceramic can be seen.

Composites with graphite additives have the worst electrical conductivity because of the size and shape of the mixed graphite grains. In case of CNT additives the observed higher conductivity with lower carbon nanotube content needs further investigations. We think that between the nodules only few current paths may be involved in conductivity process because of the nodulation of the CNTs. In case of higher CNT content it is more likely that agglomerated CNTs occur and it is not sure that they are connected (Fig. 3). Furthermore the crystallisation and grain grow of β-Si_3N_4 particles may inhibit the bridging of CNTs.



a) b)

Figure 1. Multilayer contacts (a) and measurement system (b)

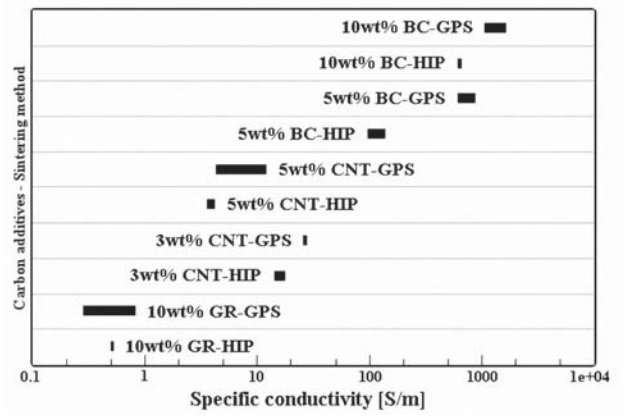
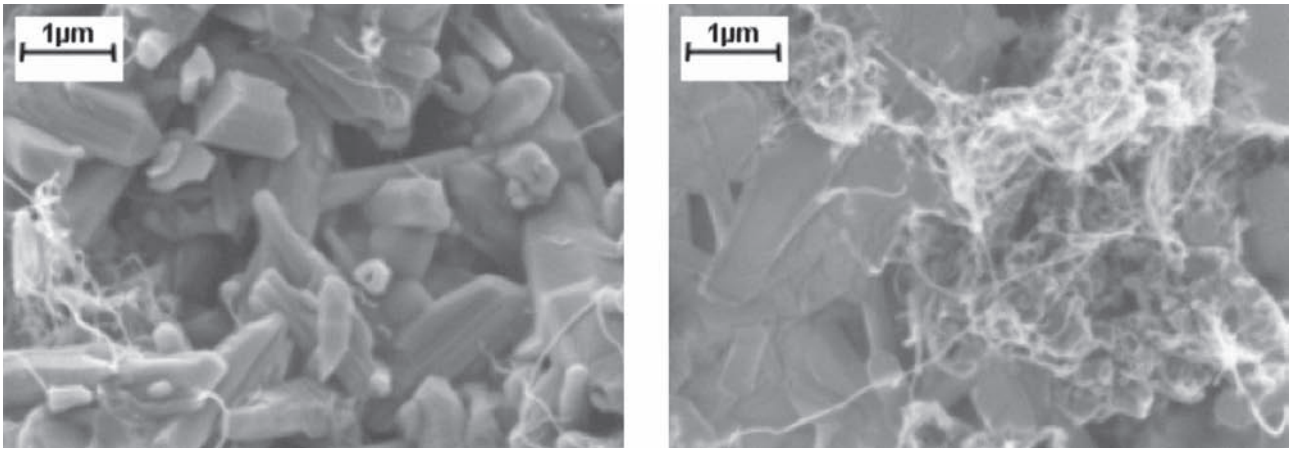


Figure 2. Specific conductivity range of conductive composites

The highest conductivity was reached with black-carbon additives because the nano sized black-carbon has been found to build in bunchy, chainy cluster forms.

In the case of GPS sintering we obtained higher conductivity than in the case of HIP. In case of HIP technique the higher sintering pressure and the holding time support the β-Si_3N_4 formation (Fig. 4). The bigger grain size of β-Si_3N_4 decreases the formation of the percolation network. Furthermore, it can generate the crumbling and decomposing of the conductive clusters, so further decreasing can take place in the conductivity.

If electrical conductive AlN phase is mixed to the base ceramic (B type), increasing conductivity can be experienced (Table 2). It means that addition of the conductive AlN phase may further improve the electrical conductivity of composites.



a) b)

Figure 3. Fracture surfaces of CNT reinforced composites sintered by HIP technique with 1 wt% CNT (a) and 5 wt% CNT (b)

Table 2. Specific conductivity of 5 wt% CNT samples with different base ceramic

Sample No.	Base ceramic	Sintering method	Specific conductivity [S/m]
1A	A	GPS	7.19
2A	A	GPS	5.58
3A	A	GPS	4.31
4A	A	GPS	12.09
5A	A	GPS	7.51
1B	B	GPS	356
2B	B	GPS	9.36
3B	B	GPS	132
4B	B	GPS	129.5
5B	B	GPS	36.3

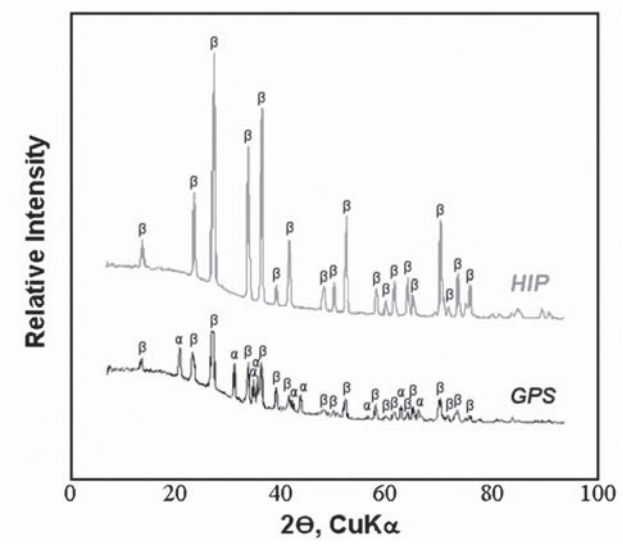


Figure 4. X-ray diffractograms of 1 wt% CNT composites made by different sintering method

IV. Conclusions

The addition of carbon parts to silicon nitride ceramics drastically changes the electrical properties of the composites. Thus, excellent conductive materials can be produced from the insulators using different type and concentration of carbon additives.

In the investigated composites the electrical conduction intervenes in percolative way. In case of graphite addition percolation threshold is above 5 wt%, and at 10 wt% low DC conductivity was found. These results may be attributed to the grain size and shape of the graphite. The highest conductivity was reached with black-carbon additives because the nano-sized black-carbon has been found to build in bunchy, chainy cluster forms. In case of CNT additives electrical conduction appeared at 3 wt%. Increasing of the CNT content does not mean higher electrical conductivity because of the nodulation of CNT fibers. Furthermore increasing the CNTs content in the well-grown β-Si_3N_4 derogates the connection between the CNT nodules so the conductivity of the main composite material decreases. The reason of it is that β-Si_3N_4 grain grows during the sintering.

Composites that are prepared on low pressure by GPS sintering have better conductivity than the high pressured HIP sintering because of the more β-Si_3N_4 formation. The grain size of β-Si_3N_4 is effectively bigger than the grain size of α-Si_3N_4 therefore blocks the conductive network formation.

Adding the conductor AlN did not cause the improvement of percolation limit in the examined compositions, but increased the electrical conductivity of the originally conductor composites forming more electrical connections between the conductive parts.

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