Polymer composites with non-stoichiometric titanium carbides

A. V. Ishkov and A. M. Sagalakov
Altai State University, Barnaul

In an earlier work we investigated conductive polymer composites (CPCs) based on bismaleinimide binder PAIS-104 [1]. Electrical conductivity of materials was achieved by introducing non-stoichiometric titanium carbides TiN$_x$ (where $0.5 \leq x < 1$) obtained by self-propagating high-temperature synthesis (SPHTS) from metallic titanium and nitrogen and possessing metal conductivity [2].

The use of the indicated conductive fillers made it possible to produce CPCs with characteristics superior to those of known materials of similar designation. The electrical conductivity of the material obtained is 1–2 orders of magnitude higher than that of its analogues, and varies widely depending on the content and nature of the filler [3]. Furthermore, the CPCs produced exhibit a new property – the effect of self-regulation. The temperature dependence of electrical conductivity of the material is characterised by the presence of an inflection at a temperature of 75–85°C. All this makes the studied materials promising for the production of conductive coatings, heat and radiation screens, current collectors, grounding electrodes, etc. [4]. However, a considerable shortcoming of such CPCs is the difficulty of producing titanium nitride of the prescribed composition, since SPHTS with the participation of gaseous substances depends greatly on the hydrodynamic parameters of the gas flow through porous layers of the solid substance.

At the same time, other similar compounds, for example, titanium carbides, can be conductive fillers for CPCs. Like non-stoichiometric nitrides, they are conductive and also can be easily produced by the direct interaction of substances. In this case, the SPHTS reaction proceeds in solid phase, and the composition of the product is easily reproduced [5].

The aim of the present work is to produce CPCs based on PAIS-104 and non-stoichiometric titanium carbides and to investigate their properties.

EXPERIMENTAL PROCEDURE

The binder used – PAIS-104 in accordance with the TU 6-05-231-192–79 specification – comprised an oligomer with an average molecular weight of $3.5 \times 10^3$ (viscometry) with a content of free amine groups of 4.8%, a drop point of 103°C, and a gelation time of 180 s. To remove unreacted monomers, the binder powder was washed with a 5% solution of HCl, with a soda solution, and then with water, until neutral. The polymer was dried in an exsiccator.

PAIS-104 fraction with $d < 100 \mu$m was used.

The fillers were produced by the interaction of power titanium of grade PTK with carbon black of grade PM-50 in a SPHTS regime in an argon atmosphere. The SPHTS reaction was initiated by a thermite composition (Al:Fe$_2$O$_3$).

The composition of non-stoichiometric carbides was confirmed by X-ray diffraction analysis (DRON-2 diffractometer, CoK$_\alpha$ radiation) and chemical analysis. To produce the composites, use was made of titanium carbide fraction $d < 100 \mu$m. The specific surface of the fillers was determined from the adsorption of surfactants.

The composites were produced by hot pressing of a mixture of filler and binder powders, prepared in a two-cone mixer, using a well-known regime [6] at a pressure of 20–30 MPa and a temperature of 200–220°C for 1 h and at 240–250°C for 1 h.
The density of the specimens was determined by hydrostatic weighing. The electrical conductivity was measured by the potentiometric method after the metallisation of specimens of known formula. The structure of the materials was investigated by scanning microsections of specimens and determining the fractal dimension of the filler boundaries by means of an original computer program.

RESULTS AND DISCUSSION

As indicated above, a feature of SPHTS is the dependence of the composition and properties of the materials obtained on a combination of different factors: the initial temperature, the combustion rate, the fineness of the materials, etc., and therefore it is necessary to monitor the properties and characteristics of the materials produced each time. Carbides were produced by burning mixtures of simple substances taken in a Ti/C molar ratio of 1:0.5, 1:0.6, 1:0.75, and 1:0.9.

Table 1 gives the main physicochemical characteristics of the fillers. As can be seen from the given results, the prescribed composition of carbides was well reproduced during synthesis. The products produced are in fact non-stoichiometric titanium carbides with a developed surface, the composition of which can be expressed by the formulae TiC0.5, TiC0.6, TiC0.75, and TiC0.9 respectively. This makes them more promising conductive fillers than the non-stoichiometric titanium nitrides studied earlier.

The fractional composition of the carbide powders used is given in Table 2. To determine the fractional composition, 10% suspensions of powder fillers in glycerin were prepared, after which a coat of suspension was applied to the glass of a scanner with a resolution of 4800 dpi. The proportion of fractions was determined by counting the number of particles of the same size on a scanned micrograph of the suspension and relating it to the total number of particles in the field of view. The use of a scanner with such a resolution makes it possible to distinguish particles with a size down to 5 µm size with confidence.

The procedure indicated was used to determine the densities of the CPC specimens obtained, and the dependence of density on filler content was studied. The dependence of the density of the materials obtained on their content of non-stoichiometric filler is given in Figure 1.

![Figure 1. Dependence of density (1–3) and porosity (1'–3') of composite materials on proportion of filler: 1 – TiC0.75; 2 – TiC0.5; 3 – TiC0.9](image)

<table>
<thead>
<tr>
<th>Table 1. Physicochemical characteristics of fillers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>TiC0.5</td>
</tr>
<tr>
<td>TiC0.6</td>
</tr>
<tr>
<td>TiC0.75</td>
</tr>
<tr>
<td>TiC0.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Fractional composition of fillers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>TiC0.5</td>
</tr>
<tr>
<td>TiC0.6</td>
</tr>
<tr>
<td>TiC0.75</td>
</tr>
<tr>
<td>TiC0.9</td>
</tr>
</tbody>
</table>
As can be seen from the given dependence, there is a consistent increase in the density of the CPC specimens obtained as their carbide content increases, beginning from 20% (9 vol.%) up to a heavily filled material. As in the case of previously studied materials with titanium nitrides, there is a divergence between the true density of the CPC and its theoretical magnitude calculated on the assumption of additivity by means of the formula

\[ d_{\text{meas}} = d_f \times \alpha + d_p \times (1-\alpha) \]  

(1)

where \( d_f \) is the density of the filler (g/cm\(^3\)), \( \alpha = d_f \times \omega / [d_f - \omega \times (d_f - d_p)] \) is the volume fraction of filler in the CPC, \( \omega \) is the mass fraction of the filler, and \( d_p \) is the density of the pure polymer (g/cm\(^3\)).

This divergence is observed in materials containing 25% (14 vol.%) filler and increases subsequently. It is interesting to note that the divergence between the theoretical and experimental density of CPC is dependent on the composition of carbide, since the specific surface of carbides of different compositions is roughly the same. Such behaviour of the density of materials indicates pore formation in the studied composites and other interactions in the system.

The dependence of the porosity of CPCs on their filler content (Figure 1) can be explained using the model proposed earlier by the present authors [7].

The model is based on evolution of the pore structure in the material. Thus, in a lightly filled composite, the pores will be localised close to filler particles and out of reach of external factors. This region of the CPC structure is bounded by the volume fraction of non-stoichiometric filler from 10–15 to 35–45% (20–60 wt.%) – region a. With further increase in the filler content, in accordance with known models of composite materials, linking of regions of surface-modified polymer surrounding the filler will occur, which in the present case will cause a certain reduction in porosity (region b). In this region, pores surrounding individual particles form an inconstant system with partial emergence on the surface. The concentration boundaries of this region correspond to a filler proportion of 45–75 vol.% (60–80 wt.%). Finally, in a heavily filled CPC with a shortage of binder, a constant developed system of pores emerging on the surface is formed (region c), and here the nature and arrangement of the pores differ considerably from the two previous regions. In this region the material is capable of maximum interaction with external factors through the system of pores. The lower boundary of this region corresponds to a volume content of non-stoichiometric filler above 75% (>80–85 wt.%). In [7] this model was checked against the concentration dependence of water absorption of the CPC. The composition dependences of the indicated characteristics for TiC\(_0.6\)-based material are similar to those presented in Figure 1.

In the present work a study was made of the dependence of the fractal dimension of the boundaries of the filler, \( D \), on the composition of the CPC, and, again, the results were compared with the proposed model. The fractal dimension was determined by two methods: the section island method (SIM) and the cell counting method (CCM) [8]. In the former case, the fractal dimension is calculated from the ratio of the perimeter of filler boundaries to the area covered by them on the microsection image of the specimen:

\[ P(\delta) = c\delta - D(S(\delta))D / 2 \]  

(2)

where \( P(\delta) \) and \( S(\delta) \) are the perimeter and area of the closed figure, calculated using reference \( \delta \), and \( c \) is a constant.

In the second method, the surface is covered with a grid of known cell size, and the number of cells in which there is a boundary element of a particle or an aggregate of filler is counted (see expression (3)). Presenting the dependence of the number of cells on their size in logarithmic coordinates, the fractal dimension is found from the angular coefficient of the obtained dependence according to the least-squares method (LSM) [9]:

\[ N(\delta) \sim 1 / \delta^D \]  

(3)

where \( N(\delta) \) is the number of cells on size \( \delta \) into which a boundary element of the subject entered.

Taking into account the specific nature of the procedure used, it is not the true magnitudes of the fractal dimension that are determined but the directly related fractal characteristics of a plane image of the subject [8].

Fractal dimensions determined both by the SIM and by the CCM for the investigated specimens proved to be similar and were processed together.

As can be seen from Figure 2, in lightly filled specimens (region a of the model), up to a content of ~45 vol.% filler, the fractal dimension is higher than the topological, i.e. the structure of the filler agglomerates in the CPC is fractal, and \( D \) depends on composition. Starting with a 20–25% content of carbide, this quantity increases sharply: a percolation transition \( a \rightarrow b \) occurs, and the structure again is stabilised up to a filler content of 60–70%. Then, for composites containing 75% titanium carbides and above, a sharp increase is again observed in quantity \( D \), which is connected with the transition of the structure of the CPC into region c.

Thus, investigation of the fractal dimension of the grain boundaries and their agglomerates showed goodness of fit of the proposed model and made it possible to determine more accurately the boundaries of the concentration regions and to establish the presence of clear percolation transitions. The lower boundary of region a amounted to 20–25% (9–15 vol.%). Then, from
20–25 to 30% (in some cases up to 40%) of the structure of the material changes sharply: the first percolation transition into region \( b \) occurs, which stretches up to 60–70% (45–55 vol.%), and then a second transition into region \( c \) is observed (70–75%), which begins with an 80% (65 vol.%) content of conductive filler.

The existence of a certain relationship between the fractal dimension of the filler boundaries in the CPC and its composition should be pointed out, and also the relationship between the extent of the boundaries of percolation transitions, especially the \( a \rightarrow b \) transition, and this quantity. As can be seen from Figure 2, the greatest values of the fractal dimension are characterised by CPCs based on carbide \( TiC_{0.75} \) (from 1.150 to 1.357). The percolation transition boundaries are also more pronounced for these materials. For compositions based on \( TiC_{0.5} \), the fractal dimension of the filler boundaries is lowest (1.050–1.135), and the \( a \rightarrow b \) transition stretches almost to a 40% carbide content. Compositions with \( TiC_{0.6} \) and \( TiC_{0.9} \) occupy an intermediate position.

By a known procedure \[10\], the volume resistivity of obtained CPCs at 25°C was measured by the potentiometric method. The dependence of the volume resistivity of CPCs is given in Figure 3. It can be seen that it has a typical S-shape \[4\].

As follows from Figure 3, with increase in the content of non-stoichiometric filler, there is a consistent decrease in the resistance of the CPC. In the region of a low content of conductive fillers, the materials produced are characterised by a resistance value greater than unity. On transition of the structure of the CPC into region \( b \), the resistance of the material falls sharply. A second sharp jump in resistance occurs on transition of the filler content boundary of 70–75%. The structure of the material corresponds to region \( c \) of the proposed model.

Since the fillers investigated have a developed surface and possess an increased reserve of surface energy owing to their non-stoichiometry, by the instant of achievement of a non-stoichiometric filler content of 20–25% (region \( a \)), stable conductive structures of filler particles surrounded by a film of surface-modified polymer have already formed in the material.

On transition from region to region, there is a sharp fall in resistance, which indicates the formation of conductive structures of different types. Here, not only an increase in the content of conductive filler but also its polydispersion evidently appear (Table 2). In transition region \( b \) (Figure 2), the morphology of the conductive structures, from positions of synergistics, must already be regarded as bifractal (here, it is not the strict mathematical term that is used, but rather the existence in different regions of the model of self-similar figures with a different value of \( D \)). On the one hand they comprise a fractal of particles of region \( a \) (\( D \) from 1.050 to 1.100), and on the other hand structures arise that are formed by direct contacts between filler particles of coarser size. The growth and evolution of a fractal characteristic of region \( c \) begins, with a much higher value of the fractal dimension (\( D \) up to 1.370). The appearance in the structure of a second fractal causes a sharp fall in resistance. Subsequently, it is in region \( c \) that we have a structure formed by the interpenetration of two fractals. Naturally, for materials similar to the investigated fillers containing particles differing strongly in size, the conductive structure must be considered to be polyfractal (in the same sense as above). The existence of structures of this type is borne
out by the fact that CPCs belonging to regions a and b obey Ohm’s law, i.e. the mechanism of conductivity in these materials is a contact mechanism. The volume resistivity values determined from the volt-amperograms of the studied materials coincided with those obtained earlier.

For the CPCs obtained, an investigation was made of the temperature dependences of electrical conductivity in the range 25–110°C. Figure 4 gives the temperature dependences of electrical conductivity of CPCs with TiC_{0.75} carbide.

The electrical conductivity of the obtained CPCs based on titanium carbides belongs to the metallic type. The temperature dependences of electrical conductivity for the CPCs obtained in the first and the subsequent cycle do not differ. The results obtained indicate that the process that causes a sharp change in electrical conductivity is reversible, while the electrophysical characteristics of the materials are stable.

Materials containing 25–70 wt.% filler are characterised by a non-linear temperature dependence of electrical conductivity in the region investigated. In the temperature range 80–95°C there is a sharp increase in the thermal resistivity, termed the self-regulation effect [11], which is caused by thermal relaxation in the interlayers of the surface-modified polymer and by rearrangement of the conductive structures. This effect does not appear in heavily filled specimens.

The composition of the fillers has a certain influence on self-regulation of the CPCs obtained. Thus, the range of self-regulating transition in a CPC based on TiC_{0.75} is widest and extends from 78 to 90°C. For material based on TiC_{0.5}, a jump in resistance is observed at 85–95°C. Such a transition for CPCs with TiC_{0.6} and TiC_{0.9} occurs at 80–90 and 87–92°C respectively. The absolute magnitude of the jump in resistance also depends on the filler (Figure 3).

Thus, on the basis of binder PAI-104 and non-stoichiometric titanium carbides TiC_x (where 0.5 ≤ x < 1), conductive composites with reproducible characteristics can be produced.

The density, porosity, and fractal dimension of the filler boundaries of the materials produced are dependent upon the proportion of filler in accordance with the proposed model of change in the structure of the conductive material. The structure of the material must be considered to be polyfractal.

The concentration dependence of the resistance of the obtained materials is S-shaped. As the filler content increases, there is a gradual change in the type of basic conductive structure.

In a study of the temperature dependence of the electrical conductivity of the materials produced, the effect of self-regulation was found for CPC specimens containing 25–70% non-stoichiometric filler. The electrical conductivity of the materials changes according to the metallic type. Self-regulation in CPCs depends on the content and composition of the filler.

REFERENCES
