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Electro-Conductive Composites Based on Metal Oxides and Carbon Nanostructures

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Optimal conditions were found for the formation of carbon-oxide composites by the treatment of mixtures of oxides of aluminum or titanium with carbon nanotubes and nanofibers in a planetary ball mill. The dependences of the electrical conductivity of composites on the content of carbon nanomaterials (1-5% by mass) were determined. It is shown that the addition of 3%(wt) of CNT to the oxides leads to a sharp increase in the electrical conductivity: from 5.0×10^{-8} to 2.8×10^{-4} S/cm for Al_2O_3 and from 5.0×10^{-6} to 2.2×10^{-2} S/cm for TiO_2. It was shown that the carbon-oxide composites are promising carriers of the catalysts of electrode processes in electrochemical devices. It was revealed that Pt/TiO_2 - CNT catalyst containing 5% (mass) of carbon nanotubes has the best catalytic activity in oxygen reduction, in an electrode-modeling cathode of a fuel cell.

Keywords: Carbon nanotubes, Carbon-ceramic nanocomposites, Electrical conductivity, Catalytic activity.

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1. INTRODUCTION

Composites based on ceramics and carbon materials have wide prospects for the modern industry [1-5]. Of certain interest is to use carbon nanotubes as modifying components. Thus the high thermal conductivity of nanotubes suggests that their introduction to the ceramic material, even in small amounts, would improve thermal conductivity and resistance to thermal shock [2]. The electrical conductivity of such composites can be useful for creating various electrochemical devices [3]. Thus, to give conductive properties through the introduction of small additions of carbon nanomaterials is attractive compared to other composite systems.

In the production of electrically conductive composites with the dielectric matrix and conductive filler there are of particular importance the intrinsic conductivity of the filler particles, the amount of injected filler, as well as the shape of the filler particles. Currently, a huge number of composites based on Al_2O_3 [4-8], Si_3N_4 [8, 9], SiC [10], SiO_2 [11], TiO_2 [12-14], ZnO [14, 15], TiN [16], ZrO_2 [17] etc. are investigated. At the same time one use carbon black, nanofibers, multiwall and single-wall nanotubes, and graphene structures as fillers [4-20].

To create high-performance composite materials is necessary to introduce additives, which will either improve the properties of the base material, or give it new ones, but it is important to maintain existing properties. Therefore, to achieve the best effect it is necessary to introduce a minimum amount of additives, which give new properties to composites. In the literature data studied by us the content of carbon materials in the composites ranged from one percent to several tens of percent. In this connection, one of the problems is the determination of the minimum content of carbon in the composite material that provides the desired properties.

The aim of this work is to obtain conductive carbon-oxide composites based on Al_2O_3 and TiO_2, and study the dependence of the specific conductivity of composites on the conditions of their formation and types of carbon nanostructures (CNS).

2. EXPERIMENTAL

We used powders of TiO_2 (anatase and rutile mixture), and γ-Al_2O_3. In order to form composites carbon nanofibers were obtained with diameters of 100 – 200 nm, multiwalled nanotubes with diameters of 10 – 50 nm, as well as thin tubes with diameters of 5 – 10 nm. Carbon-ceramic composites were prepared by mixing carbon nanostructures with metal oxides in a planetary ball mill. Such parameters as rotation speed, milling time, type and mass content of the CNS were varied.

The structure and phase composition of the samples were investigated by transmission electron microscopy on instruments EMW–100B and JEOL JEM–100 CX. In order to study the surface of the composites we used a field emission scanning electron microscope Zeiss LEO SUPRA 25, equipped with EDX attachment for X-ray microanalysis of the elemental composition of the sample surface. X-ray analysis of the samples was carried out on a powder diffractometer DRON–UM2. Thermogravimetric analysis of the samples was performed on the instrument STA 409C LUXX. To measure the specific surface area an analyzer QUADRASORB SI was used. Electrical conductivity of the materials was determined on a potentiostat P–30S (Elins Co). We used four- and double- zoned cells with electrodes 0.5 and 0.3 cm in diameter.

In addition, to the surface of the obtained composite materials platinum clusters were deposited and their electrocatalytic activity in oxygen reduction was investigated. Tests were conducted with the cathode electrode of fuel cell modeling. Cyclic volt-ammograms recorded at various speeds with the potential sweep blowing air through gas-conducting channels. After registration, the cyclic volt-ammograms stationary currents in potentiostatic mode were recorded. For this we used potentiostat P–30S and impedancemeter Z–500PX (Elins Co).

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3. RESULTS AND DISCUSSION

To investigate the dependence of conductivity on the content of carbon nanomaterial mixtures containing from 1 to 5%(wt) of CNTs were prepared. After processing in a planetary ball mill the samples of oxide powders and nanotubes had a homogeneous appearance, however, at the study by electron microscopy in mixtures containing 1% and 2%(wt) CNTs, the tubes on their own are almost not observed. At the content of 3%(wt) as bundles of nanotubes, as well as individual tubes could be observed. At the content of 5%(wt) a large number of nanotube bundles, distributed between the oxide particles were observed. This pattern was observed in the case of aluminum oxide, as well as in the case of titanium oxide (Fig. 1).

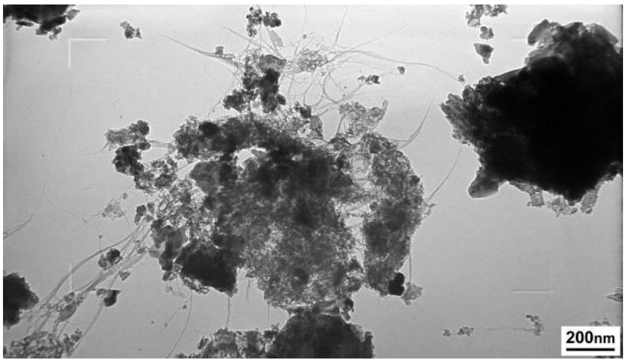

Fig. 1 – TEM image of the composite MCNT/Al_2O_3, with 5%(wt) of MCNT

We selected optimal conditions for processing time, the degree of load, type and content of the carbon nanomaterial. Investigation of the electrical conductivity of composites based on Al_2O_3 with different content of carbon nanotubes have shown that the dependence is exponential. At the content of CNT 1 – 2%(wt) the electrical conductivity remains practically unchanged and amounts to about 5×10^{-8} S/cm. The increase of the nanotubes content up to 5%(wt) leads to a sharp increase in conductivity up to 3×10^{-4} S/cm. In this case one can observe a jump of conductivity at 3%(wt) to 4.5×10^{-5} S/cm. In the case of TiO_2 this effect also occurs at 3%(wt) of CNTs and the electrical conductivity of this composite is 2.2×10^{-3} S/cm. In general, the conductivity varies from 5×10^{-6} S/cm for pure TiO_2 up to 2.2×10^{-2} S/cm for the composite containing 5%(wt) of CNTs (Fig. 2).

For selection of the optimum degree of load and milling time in the future we used a composite with 3%(wt) of carbon nanostructures. The experiments revealed that the highest conductivity of milled composites reached at 100 rpm, for 30 min (Fig. 3, 4). A further increase in time or number of revolutions leads to a refinement of carbon nanostructures and, consequently, reduces the conductivity.

At the study of the electrical conductivity of composites according to the type of carbon nanostructures, it was found that the composites with multiwall carbon nanotubes have the best conductivity (Fig. 5), the conductivity of composites with single-walled carbon nanotubes (SWNT) is worse by two orders of magnitude; a composite with carbon nanofibers (CNF) has the worst conductivity.

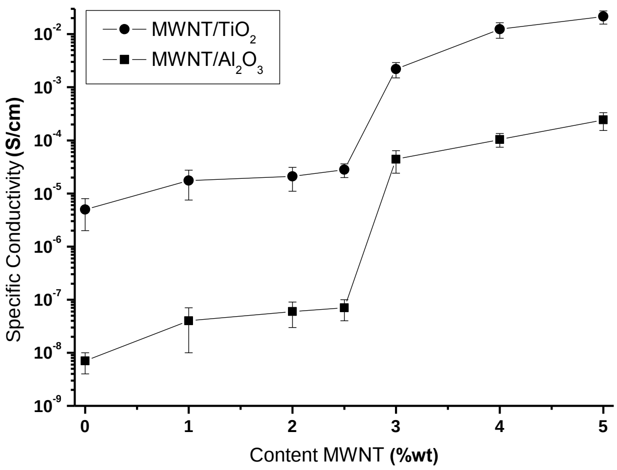

Fig. 2 – Dependence of the conductivity of the composites MCNT/Al_2O_3 and MCNT/TiO_2 on the mass content of carbon nanotubes

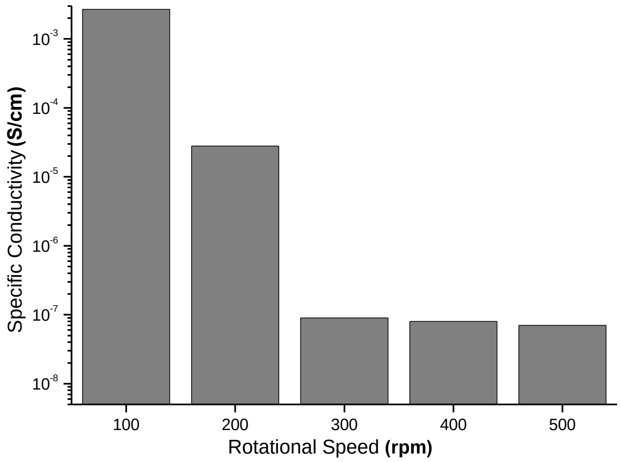

Fig. 3 – Dependence of the conductivity of the composites TiO_2/MCNT (3%wt) on the number of revolutions

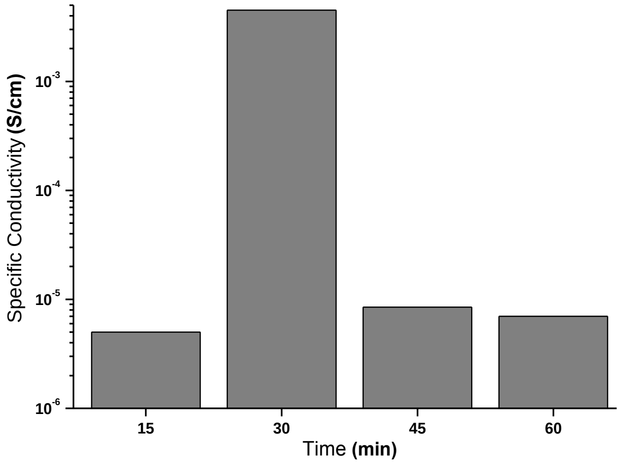

Fig. 4 – Dependence of the conductivity of the composites TiO_2/MCNT (3%wt) on the milling time

For a detailed description of the formation conditions of carbon-oxide composites in a planetary ball mill the magnitude of strain effect on the material was also determined during the machining method of the test sites and the energy transferred to the sample during ball-milling was calculated [21]. This method uses a universal value that allows one to be independent on the type of mill and sufficiently facilitates the production and optimization of the processes of formation of composite materials in conditions of a variety of grinding and mixing machines.

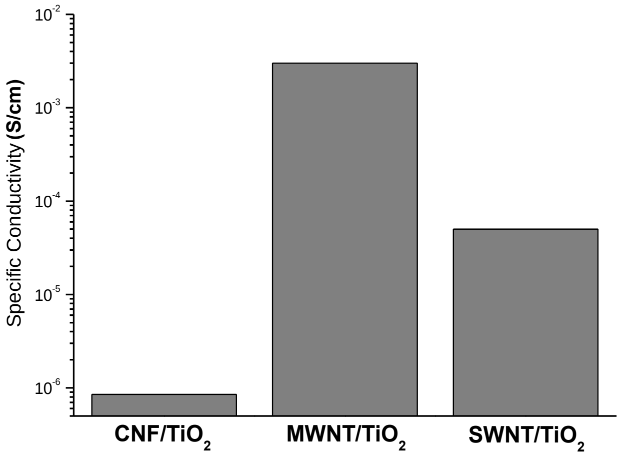

Fig. 5 – Dependence of the conductivity of the composites CNS/TiO_2 (3%wt) on the type of carbon nanostructures contained in it

According to the results of calculations of the dose of strain effect and the data of the electrical conductivity of composites plots of the dependence of electrical conductivity of composites MWNT/TiO_2 on the dose of strain effect on the samples were constructed (Fig. 6).

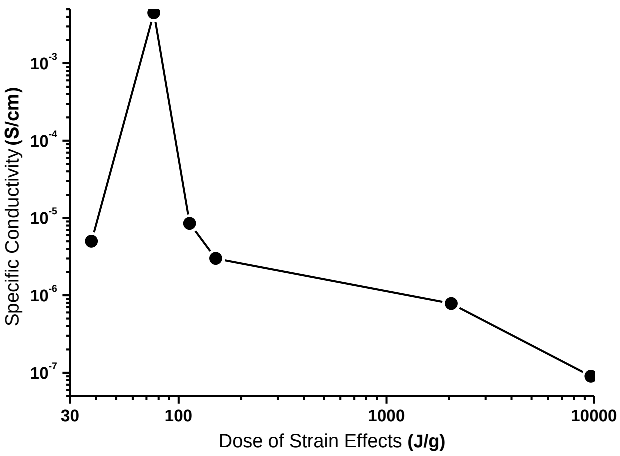

Fig. 6 – Dependence of the conductivity of the composite MWNT/TiO_2 on the dose of strain effect on the samples

As can be seen from the figure, the samples obtained by mechanical action 76 J/g have the highest conductivity (4.5×10^{-3} S/cm). Further increase of the load and processing time leads to a decrease in electrical conductivity, which is obviously due to the oxide shredding and destruction of carbon nanotubes. This assumption is confirmed by the values of specific surface area of the composites, which vary from 55 m^2/g for the composites obtained at a dose of strain effect 38 J/g to 80 m^2/g for the composites obtained at 9.6 kJ/g. A similar pattern is observed in the case of composites based on aluminum oxide.

To evaluate the effectiveness of the use of CNT/TiO_2 composite as a carrier of catalysts in electrochemical devices Pt/TiO_2-CNT samples with different contents of carbon nanotubes were prepared and their electrocatalytic activity was investigated using an electrode-modeling cathode of a fuel cell. According to scanning electron microscopy Pt particles are distributed over the surface of titanium oxide fairly evenly. The average particle size is in the range 5-10 nm (Fig. 7). According to the EDX Pt content is at a level of 10%(wt).

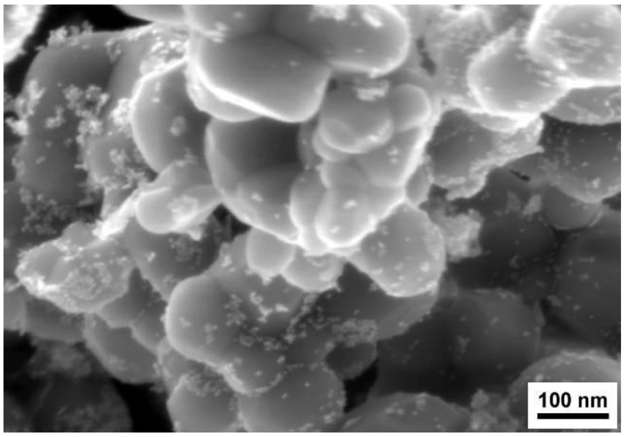

Fig. 7 – SEM image of TiO_2 with Pt clusters deposited on it

Current-voltage characteristics of the system Pt/TiO_2 – CNT with different mass content of carbon nanotubes are shown on Figure 8.

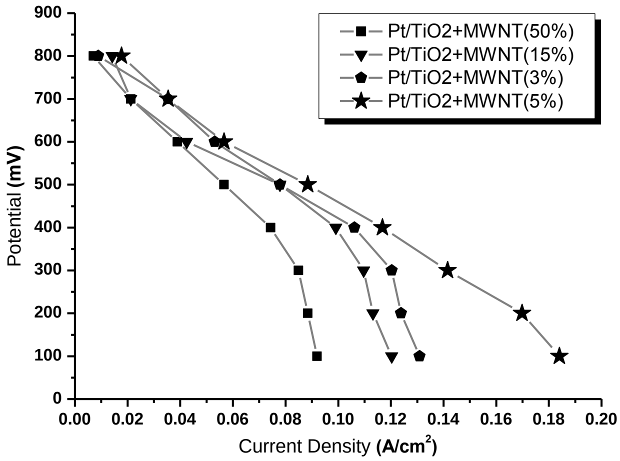

Fig. 7 – SEM image of TiO_2 with Pt clusters deposited on it

The composite with 5%(wt) of MWNT is the most effective. The composite with 3%(wt) content of CNT has lower quantity of extended carbon structures providing electron transport, and in samples with 15 and 50%(wt) of CNT the low efficiency of Pt-catalyst may be related to difficulties of contact with the reaction medium because of the large amount of carbon material.

According to literature data, at the presence of spherical particles of the conducting phase and particles of non-conductive matrix of the same size for the occurrence of the percolation the content of the conducting phase should be at the level of 50%. In the case of ellipsoidal particles this content reduces to 20-30%. For filamentous particles, this value is usually less than 10%. In the case of composites obtained by the synthesis of carbon nanostructures directly on the surface of oxide powders, apparently, there is a tight contact both between the carbon tubes and between tubes and particles of oxides.

CONCLUSIONS

Optimal conditions were determined for the formation of carbon-oxide composites by the treatment of mixtures of oxides of a metal with carbon nanomaterials in a planetary ball mill. The dependences of the electrical conductivity of composites on the content of carbon nanomaterials (1–5%wt) were determined. It is established that the addition of 3%(wt) of CNT to the oxides leads to a sharp increase in the electrical conductivity: from 5.0×10^{-8} to 2.8×10^{-4} S/cm for Al_2O_3 and from 5.0×10^{-6} to 2.2×10^{-2} S/cm for TiO_2. It was shown that the carbon-oxide composites are promising carriers of the catalysts of electrode processes in electrochemical devices. It was revealed that Pt/TiO_2 – CNT catalyst containing 5%(wt) of carbon nanotubes has the best catalytic activity in oxygen reduction, in an electrode-modeling cathode of a fuel cell.

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REFERENCES

1. *Composites: ASM Handbook* (Ed. D.B. Miracle, S.L. Donaldson) (ASM International: The Materials Information Company: 2001).
2. J.A. Arsecularatne, L.C. Zhang, *Recent Patents on Nanotech.* **1**, 176 (2007).
3. D. Eder, *Chem. Rev.* **110**, 1348 (2010).
4. Y.V. Blagoveschensky, K.V. Van, A.A. Volodin, V.M. Kiiko, A.A. Kolchin, N.I. Novokhatskaya, B.P. Tarasov, A.N. Tolstun, *Composites and Nanostructures* **1**, 30 (2010).
5. B.P. Tarasov, V.E. Muradyan, A.A. Volodin, *Russ. Chem. Bull.* **60**, 1261 (2011).
6. Yu. Fan, L. Wang *Carbon* **48**, 1743 (2010).
7. A.M. Bondar, I. Iordache, *J. Optoelectronics and Adv. Mater.* **8**, 631 (2006).
8. F-H.Su, Zh-Zh.Zhang, K.Wang, *Composites: Part A* **37**, 1351 (2006).
9. B. Fényi, N. Hegman, F. Wéber, *Processing and Application of Ceram.* **1–2**, 57 (2007).
10. G-B. Zheng, H. Sano, Y. Uchiyama, *Composites: Part B* **42**, 2158 (2011).
11. S.Q. Guo, R. Sivakumar, H. Kitazawa, Y.Kagawa, *J. Am. Ceram. Soc.* **90**, 1667 (2007).
12. J. Yu, J. Fan, B. Cheng, *J. Power Sources* **196**, 7891 (2011).
13. O.Yu. Ivanshina, M.E. Tamm, E.V. Gerasimova, *Inorg. Mater.* **47**, 618 (2011).
14. C. Martínez, M. Canle, M.I. Fernándeza, *Appl. Catal. B: Environmental* **102**, 563 (2011).
15. X.L. Li, C. Li, Y. Zhang, *Nanoscale Res. Lett.* **5**, 1836 (2010).
16. L.Q. Jiang, L.Gao, *J. Mater. Chem*. **15**, 260 (2005).
17. S.L. Shi, J. Liang, *J. Appl. Phys.* **101**, 023708 (2007).
18. Zh-Sh. Wu, G. Zhou, Li-Ch. Yina, *Nano Energy* **1**, 107 (2012).
19. B.P. Tarasov, V.E. Muradyan, A.A. Volodin, *Fullerenes and Nanostructures in Condensed Matter* (Minsk: Publishing Center BSU: 2011).
20. A.A. Volodin, D.V. Chihirev, A.D. Zolotarenko, D.V. Schur, B.P. Tarasov, *Fullerenes and Nanostructures in Condensed Matter* (Minsk: Publishing Center BSU: 2011).
21. P.Yu. Butyagin, A.N. Streletskii, *Phys. Solid State* **47**, 856 (2005).