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FEATURES OF SYNTHESIS OF COMPOSITE MATERIAL BASED ON SILICON DIOXIDE AND CARBON NANOTUBES

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Today, there are many papers showing the effectiveness of the use of carbon nanotubes as additives to composites. Their use in polymers is especially successful, but the efficiency of their use in ceramics poses many questions. The aim of the work was to study the effect of the addition of carbon nanotubes on the properties of ceramics. For this purpose, pure silica, obtained by the hydrolysis of tetraethoxysilane in an alkaline medium, was taken as a model. The obtained granules of the material were well sintered at 900 ° C and it was decided to compound this material with carbon nanotubes. Depending on the method of introducing, the result turned out to be diametrically opposite. Nanotubes introduced during the synthesis of silica played a role in the formation of silicon dioxide grains and effectively compacted the material, increasing its hardness. On the contrary, nanotubes grown in ceramic pores wedged the grain of silicon dioxide, making the material softer. In the first case, it is important to note that the synthesis of ceramics is not affected by the synthesis of nanotubes. In turn, nanotubes always affect the process of forming ceramics. This influence leads to a change in the structure of the grains of ceramics, and as a consequence of the mechanism of interaction between them, which in turn changes the density and strength of the ceramics.

In the second case, in order to grow nanotubes in the pores and cavities of the ceramic material, one must first impregnate the ceramic material with a catalyst. Thus, there is a requirement for a precursor of the catalyst – the absence of its interaction with ceramics. The second requirement is for inertness of the ceramics, both to the catalyst and to the entire synthesis process. In addition, it is necessary that the structure of the pores does not change during the synthesis, i.e. they did not close during the synthesis of nanotubes, but provided transportation of the starting materials and reaction products.

Therefore two mechanisms that affect the formation of a composite ceramic material have been described. The described composite can be used in the rocket and space industry for compounding ceramic fairings and thermal insulation.

Keywords: quartz ceramics, carbon nanotubes, composite materials.

ОСОБЕННОСТИ СИНТЕЗА КОМПОЗИЦИОННОГО МАТЕРИАЛА НА ОСНОВЕ ДИОКСИДА КРЕМНИЯ И УГЛЕРОДНЫХ НАНОТРУБОК

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На сегодняшний день существует множество работ, показывающих эффективность использования углеродных нанотрубок в качестве присадок к композитам. Особенно удачно их применение в полимерах, однако эффективность их использования в керамиках оставляет много вопросов. Цель статьи – изучение влияния добавки углеродных нанотрубок на свойства керамики. Для этого в качестве модельной среды был взят чистый *кремнезём, полученный методом гидролиза тетраэтоксисилана в щелочной среде. Полученные гранулы материала хорошо спекались при 900 °С, и было решено компаундировать этот материал углеродными нанотрубками. В зависимости от способа введения результат оказался диаметрально противоположным. Нанотрубки, вводимые в процессе синтеза кремнезёма, играли роль в формировании зёрен диоксида кремния и эффективно уплотняли материал, повышая его твёрдость. Напротив, нанотрубки, выращенные в порах керамики, расклинивали зёрна диоксида кремния, отчего материал становился мягче. В первом случае важно отметить, что на процесс формирования керамики не влияет синтез нанотрубок. В свою очередь, нанотрубки всегда влияют на процесс формирования керамики. Это влияние приводит к изменению структуры зёрен керамики и, как следствие, механизма взаимодействия между ними, что, в свою очередь, меняет плотность и прочность керамики.*

Во втором случае, чтобы вырастить нанотрубки в порах и полостях керамического материала, нужно прежде напитать керамический материал катализатором. Таким образом, возникает требование к прекурсору катализатора – это отсутствие взаимодействия его с керамикой. Вторым требованием, очевидно, будет являться требование к инертности керамики, как к катализатору, так и ко всему процессу синтеза. Кроме того, необходимо, чтобы в процессе синтеза не менялась структура пор, т. е. они не закрывались в процессе синтеза нанотрубок, а обеспечивали транспорт исходных материалов и продуктов реакции.

Таким образом, были описаны два механизма, влияющие на формирование композитного керамического материала. Описываемый композит может быть использован в ракетно-космической отрасли для компаундирования керамических обтекателей и теплоизоляции.

Ключевые слова: кварцевая керамика, углеродные нанотрубки, композитные материалы.

Introduction. The unique properties of carbon nanotubes such as their strength and chemical resistance [1; 2] determine the interest in their use as an additive to various materials for the production of composites. At present time, there are a lot of works [3–8] showing the efficiency of the use of carbon nanotubes as additives to composites. Their application in polymers is especially successful [9–12], but the effectiveness of their use in ceramics leaves many questions. For example, direct mixing of ceramic particles with carbon nanotubes leads to a deterioration in the strength of a composite with an increase in the proportion of nanotubes [13] and only using them in materials with a large proportion of the amorphous phase, including glass and crystalline glass [14], increases the strength of such a composite.

Materials used and experiment. Carbon nanotubes were obtained from ethanol [15] on a $[Ni (NH_3)_6]Cl_2$ precursor at a temperature of 600 °C.

As a model ceramics, we used quartz ceramics produced from a slurry of aqueous ammonia and tetraethoxysilane obtained by annealing in colloid suspension. The structure of such ceramics is grains of amorphous SiO_2 (fig. 1) with the size of 200–500 nm. Ceramic material was obtained by hydrolysis of tetraethoxysilane followed by sol-gel precipitation and annealing at 900 °C.

Since the efficiency of direct mixing of nanotubes with ceramic particles does not always give an effective result, and it is very difficult to achieve uniformity of distribution of nanotubes in this case, the authors used only two methods, which guaranteed uniform mixing. On the one hand, carbon nanotubes can get into ceramics during its formation from a suspension, and on the other hand, carbon nanotubes can already be placed in ceramics by growing them in pores and cavities of the material.

To implant nanotubes into ceramics at the growth stage, the following method was used. The nanotubes were dispersed by ultrasound in 2-propanol to obtain a stable colloid. Then dispersion containing 0.1 mas. % of nanotubes was added to tetraethoxysilane in a volume ratio of 1:10, respectively. After that, ammonia was added to the mixture, and the suspension was recieved by agitation. The suspension, after drying, was annealed at 900 °C.

The growth of nanotubes in ceramics was provided by introducing a catalyst into the pores of ceramics annealed at 900 °C and was carried out at a temperature of 600 °C from ethanol. The catalyst was added into ceramics by impregnating the finished material with a precursor.

Results. In fig. 2 photographs of received materials are presented. On the left, there is a composite obtained by synthesizing ceramics in a dispersion of carbon nanotubes, on the right, there is a composite with carbon nanotubes grown in the pores of ceramics.

As you can see, with the same amount of substance, completely different volumes of material are obtained. It should be noted that the density of ceramics obtained by synthesis from a dispersion with carbon nanotubes is less than without nanotubes (or with nanotubes grown in the pores of the finished ceramics). This decrease in density is determined by the addition of carbon nanotubes during the synthesis of ceramics and is explained by the fact that carbon nanotubes, having a high specific surface, lower the free energies of the formation of ceramics on their surface. Thus, they act as a catalyst for the growth of ceramics.

Measuring the hardness of ceramic composites clearly indicate the hardening of ceramics obtained on carbon nanotubes, compared with the original, at the same time, the growth of carbon nanotubes reduced the strength of carbon nanotubes (see table).

Vickers ceramic hardness

Type of ceramic	Vickers hardness number
Without CNT	300 MPa
Ceramics made with carbon nanotube dispersion	1 GPa
Ceramics with CNT grown in pores	200 MPa

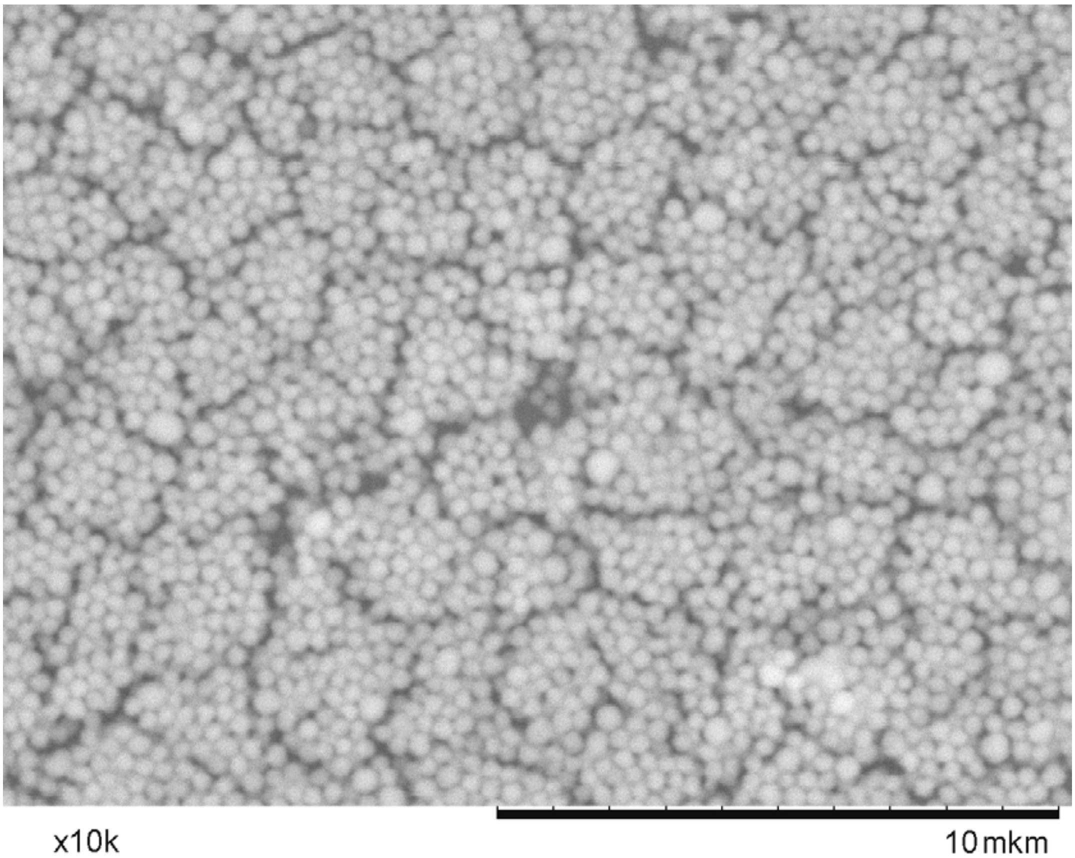


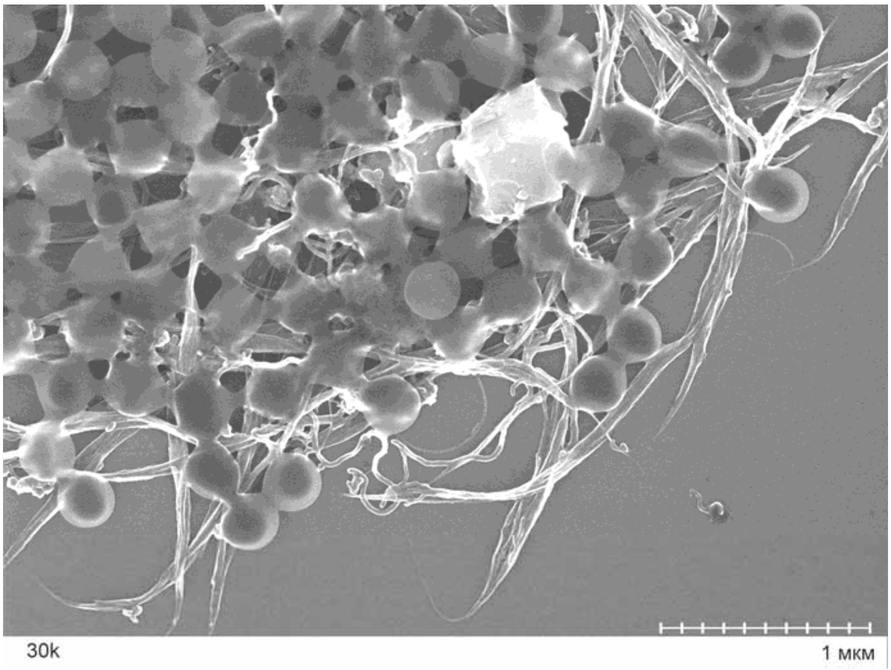
Fig. 1. Quartz ceramics. Scanning electron microscopy

Рис. 1. Кварцевая керамика. Растровая электронная микроскопия

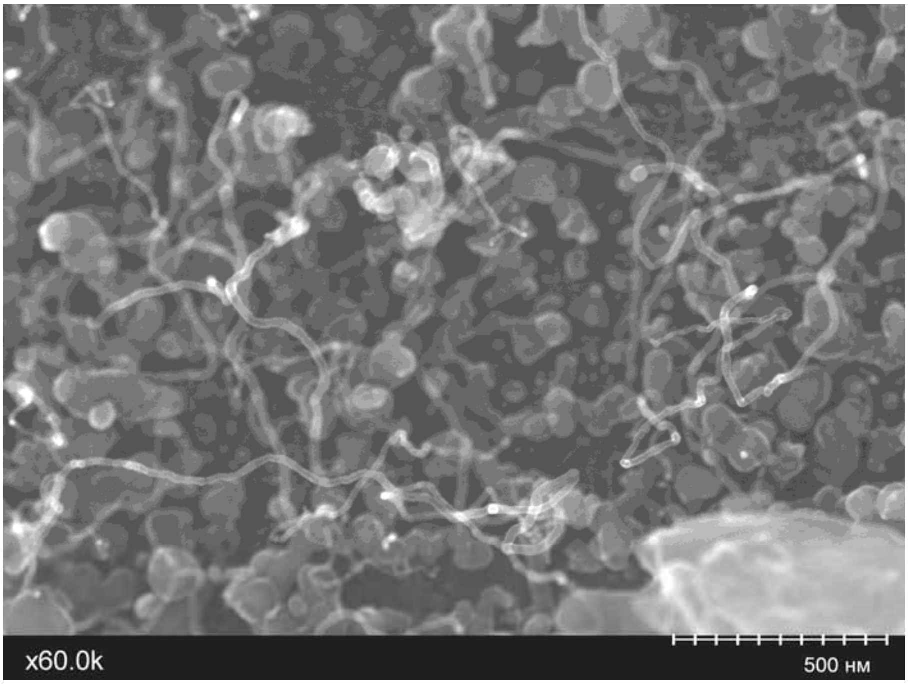
Fig. 2. Quartz ceramics, the samples of equal mass. On the left there is a composite obtained by synthesizing ceramics in a dispersion of carbon nanotubes, on the right there is a composite with carbon nanotubes grown in ceramic pores

Рис. 2. Кварцевая керамика, образцы равной массы. Слева – композит, полученный синтезом керамики в дисперсии углеродных нанотрубок, справа – композит с углеродными нанотрубками, выращенными в порах керамики

A significant increase in the hardness of ceramics grown on the basis of carbon nanotubes (fig. 3, *a*) is explained by the more dense structure of the original ceramic grains, which was created by a matrix of carbon nanotubes. That is in the colloid, the formation of silica particles proceeded not only in volume, but also on the surface of carbon nanotubes, which led to a significant compaction of the entire material after annealing.



a



b

Fig. 3. Composite based on quartz ceramics:
a – ceramics obtained with carbon nanotubes; *b* – ceramics with grown carbon nanotubes in it

Рис. 3. Композит на основе кварцевой керамики:
а – керамика, выращенная на основе углеродных нанотрубок;
б – керамика с выращенными углеродными нанотрубками

The decrease in the hardness of ceramics with carbon nanotubes grown (fig. 3, *b*) compared to the initial one can be explained by the deformations in ceramics that occur with the growth of carbon nanotubes, which have a wedging effect on grains.

Conclusion. In this work, carbon nanotubes were placed in ceramics either during its formation from a suspension, or by growing them in pores and cavities of ceramics.

In the first case, it is important to note that the synthesis of nanotubes does not affect the formation of ceramics. Nanotubes always influence the process of forming ceramics. This influence leads to a change in the structure of the ceramic particles, and as a result of the mechanism of interaction among them, which changes the density and strength of ceramics.

. In the second case, in order to grow nanotubes in the pores and cavities of a ceramic material, you should first saturate the ceramic material with a catalyst. Thus, there is a requirement for a catalyst precursor – the lack of its interaction with ceramics. The second requirement is the inertness of ceramics, both to the catalyst and to the entire synthesis process. In addition, it is necessary that the pore structure does not change during the synthesis, i.e. they did not close during the synthesis of nanotubes, but provided the transport of starting materials and reaction products.

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