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Preparation of Al₂O₃/MWCNT Composite from Nanoscale Al₂O₃ Powders and Its Mechanical Properties

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Abstract

Composite materials based on α -alumina reinforced by carbon nanotubes were prepared. The synthesis of the material was performed by mechanochemical mixing of Al₂O₃ nanoparticles with pre-ultrasonicated 0.5–3 mass % multiwall or single-wall nanotubes. The resulting pressed powder was characterized by a uniform distribution of nanotubes. Material consolidation was carried out by cold isostatic pressing and vacuum sintering followed by hot isostatic treatment at 200 MPa pressure and temperatures not higher than 1520 °C. The density of the resulting composite material was close to theoretically possible, however, nanotubes were not yet destructed due to the reaction with alumina, as established. It was demonstrated that the introduction of carbon nanotubes into the alumina matrix did not contribute to the improvement of mechanical characteristics (hardness, bending strength) compared to undoped material. Apparently, this was due to a poor chemical interface at the phase boundary.

Key words: alumina, carbon nanotubes, mechanical properties, composite materials

INTRODUCTION

Multiwall carbon nanotubes (MWCNT) are widely used as nanoadditives to develop a new generation of ceramic composites with improved operating properties due to the uniqueness of such characteristics as high thermal [1, 2] and electrical conductivity [3, 4], Young's modulus [5], tensile strength [6, 7], a length/diameter ratio [8] of more than 10³ [9–16]. Ceramic composite materials based on nanoscale oxides Al₂O₃, TiO₂, ZrO₂, MgO modified by single-wall carbon nanotubes (SWCNT) or MWCNT are being intensively developed [9, 17–23]. Ceramics based on Al₂O₃ already has mechanical properties widely demanded in industry: de-

pending on the initial powder and method of producing the material, the Vickers hardness (HV) is 8–25 GPa, ultimate bending strength $\sigma_{\text{bend}} = 150\text{--}800$ MPa, ultimate compressive strength – 0.5–2 GPa [24–26]. The introduction of MWCNT into alumina matrix is considered to be a promising method to modify these characteristics [13, 27–30].

At the same time, synthesis of ceramic composites based on MWCNT is no easy task. Firstly, it is quite difficult to achieve the uniform distribution of carbon nanotubes along the ceramics volume, since tubes are prone to aggregation during preparation [31] and interweaving in the growth process [32]. Secondly, obtaining a dense material requires high temperatures, which

would involve oxide reduction with C in nanotubes.

There are several approaches that provide a reasonably uniform distribution of MWCNT in ceramic materials. It is either the formation of a composite mixture directly in the synthesis process [33–36], or intensive mixing powders with nanotubes in suspension or a dry state [37].

With the aim of preventing the chemical reaction of nanotubes with alumina and carbide formation, either the residence time of the composite at a high temperature [29] is reduced, or sintering temperature is decreased due to hot isostatic pressing (HIP) [38]. It is also obvious that consolidation temperature of ceramic composites can be decreased due to a decrease in Al_2O_3 particle size and thereby an increase in sintering activity [39]. This paper attempted to use $\alpha\text{-Al}_2\text{O}_3$ in 60–100 nm particles that have exceptionally high shapeability and sinterability at temperatures insufficient for oxide reduction with carbon during preparation of Al_2O_3 /MWCNT composite ceramic nanopowders [40].

EXPERIMENTAL

Synthesis of MWCNT was carried out in a fluidized bed reactor by catalytic gas-phase pyrolysis of ethylene in the presence of Fe–Co/ Al_2O_3 catalyst at a temperature of 680 °C [41, 42]. Catalyst impurity particles in the resulting MWCNT were removed by reflux in a 50 % HCl aqueous solution for 2 h. Afterwards, MWCNT samples were filtered off, rinsed with distilled water until neutral pH, air dried at 110 °C for 12 h. Functionalisation (carboxylation) of MWCNT was carried out by reflux in concentrated nitric acid (Reakhim JSC, Russia) for 1.5 h, then filtered off and rinsed with distilled water until a neutral pH, whereupon dried at 110 °C for 12 h [43]. According to the titration, the concentration of surface carboxyl groups was 0.8 groups/nm².

The method described in [40] was used for preparation of $\alpha\text{-Al}_2\text{O}_3$ oxide. Production of 1 mass % Al_2O_3 /MWCNT composite material was carried out in AGO-2 planetary centrifugal mill (NOVITS JSC, Russia). A mixture of MWCNT and $\alpha\text{-Al}_2\text{O}_3$ powders in the amount of 5 g were loaded into a ceramic (ZrO_2) activator and treated for 5 min at 10g acceleration by ceramic grind-

ing bodies (diameter of 3 mm) with the addition of several drops of ethyl alcohol. In some cases, OCSiAl SWCNT (Russia) treated with alumina by in isopropyl alcohol and subsequent drying with a rotary evaporator were used.

The resulting MWCNT powders were pressed in 16 mm diameter tablets and 3 mm height and in 40 × 40 × 5 mm size bars (for bending strength measurement) by dry uniaxial pressing at 30 MPa pressure and subsequent isostatic compression at 200 MPa pressure on AIP3-12-60C setup (American Isostatic Press, the USA). Tablets with SWCNT and without nanotubes were pressed only by the single-axis method at 120 MPa pressure. After pressing, the samples were sintered in SNVE vacuum oven (PRIZMA Ltd., Russia) at 10⁻⁶ mmHg pressure for 1 h. Hot isostatic pressing of the sintered samples was carried out in a graphite furnace at 1520 °C for 1 h at 200 MPa argon pressure on AIP6-30H setup.

X-ray phase analysis of the obtained samples was carried out on CuK_α radiation monochromatized DRON-4 diffractometer (Burevestnik JSC, Russia) by point scanning with a 0.01° step in the 20–70° 2 θ angle range and a 1 deg/min shooting speed. Alumina crystallite size in powders was determined using PowderCell 2.4 software with compulsory introduction of the parameters of standard samples obtained under identical shooting conditions.

High resolution electron microscopy (HR-TEM) images were obtained using JEM-2010 transmission electron microscope (JEOL, Japan) at 0.14 nm resolution and 200 kV accelerating voltage. Particle size distribution assessment was carried out using ITEM 2040 software. The number of particles used for assessment was no less than 400 pcs.

Particle morphology of the initial materials and obtained composites was studied using JSM6460-LV JEOL and MIRA3 TESCAN scanning electron microscopes (SEM). Accelerating voltage was 20 and 30 kV.

Specific surface measurements of samples were carried out using SORBI-M automated flow-through sorption plant. All samples were preliminarily subjected to heat training in the current of argon at 200 °C for 2 h. Specific surface (S_{sp}) was calculated by the BET method [44].

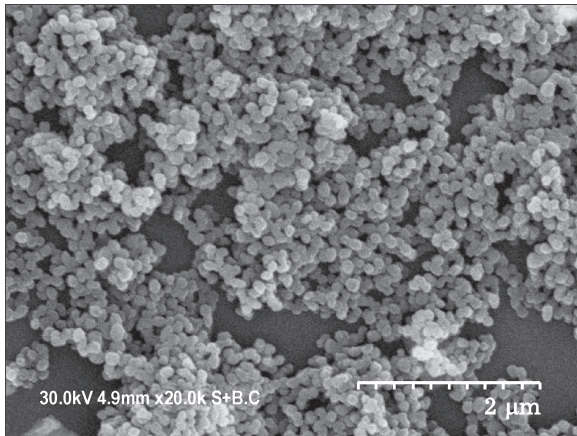


Fig. 1. Electron microscope image of initial alumina sample.

The Vickers hardness was measured using preliminarily polished samples with EMCO-TEST DuraScan 50 hardnessmeter at load on a 1 kg indenter. The bending strength was measured by three-point method using Instron 5944 testing machine.

RESULTS AND DISCUSSION

Figure 1 presents the SEM photomicrograph of the resulting alumina powders. It can be seen that particle size distribution is quite narrow, and particle shape is close to spherical. The average numerical particle size is 106 nm according to laser granulometry.

A powder diffraction pattern of alumina testifies $\alpha\text{-Al}_2\text{O}_3$ well crystallized phase with coherent scattering region (CSR) size approximate-

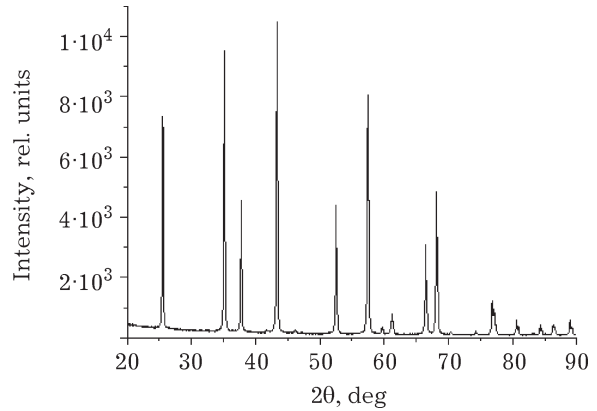


Fig. 2. Diffraction pattern of initial alumina sample.

ly equal to 100 nm, *i. e.*, the crystallite size is almost the same as the size of particles composing the powder (Fig. 2).

Large agglomerates are not observed and numerous single nanotubes are recorded in electron microscopic images of the initial sample of MWCNT (Fig. 3). Length and diameter of nanotubes distribution is narrow, the average values are 285 and 10 nm, respectively (see Fig. 3, b, c). As noted in [45], used MWCNT are characterized by high purity (sp^2 carbon fraction is over 99 %).

The MWCNT specific surface is $270 \text{ m}^2/\text{g}$, and real density is $2.05 \text{ g}/\text{cm}^3$.

From electron microscopy data from $\text{Al}_2\text{O}_3/\text{MWCNT}$ and $\text{Al}_2\text{O}_3/\text{SWCNT}$ samples, it follows that mechanical treatment does not affect Al_2O_3 particle size that is still 100 nm, and CNT are

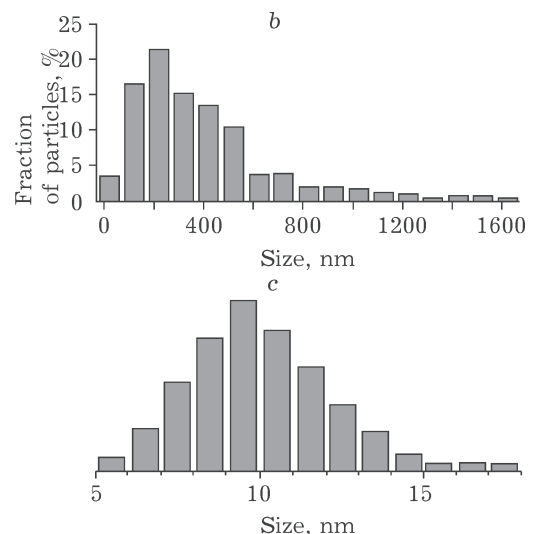
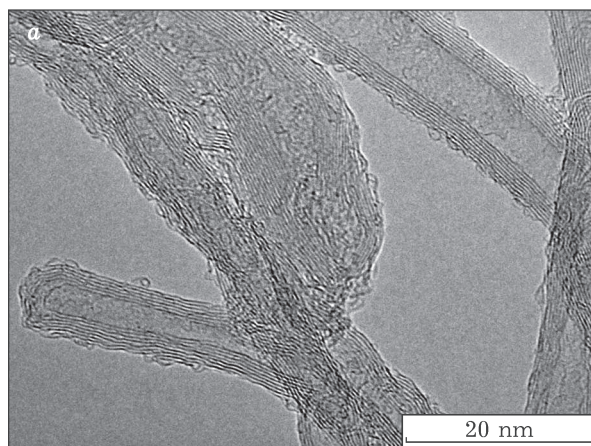


Fig. 3. Electron microscope image of MWCNT (a) and also corresponding length (b) and diameter (c) nanotube distribution.

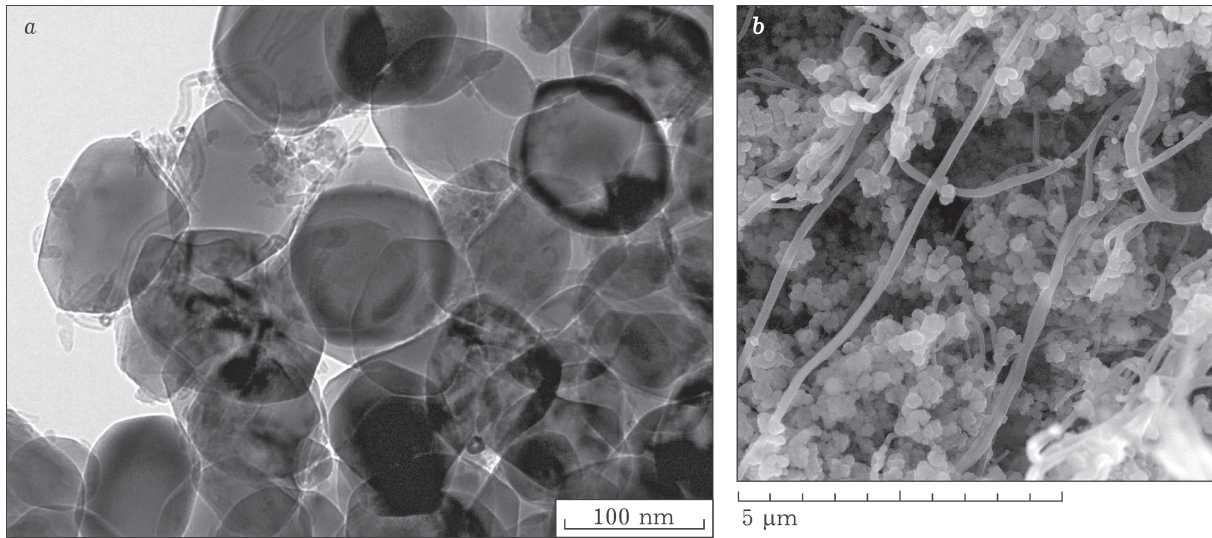
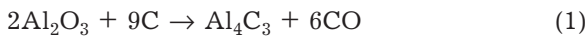


Fig. 4. Electron microscope images of $\text{Al}_2\text{O}_3/\text{MWCNT}$ (a) and $\text{Al}_2\text{O}_3/\text{SWCNT}$ (b) samples.

relatively uniformly distributed along the sample (Fig. 4). There are no large agglomerates and other clusters of CNT.

Nanotubes remain after sintering that is reaction (1) does not proceed extensively:



Perhaps, the absence of free volume in densely sintered composite prevents carbon monoxide formation shifting the equilibrium to the left.

Tables 1 and 2 present crude (ρ_0) and sintered density data for samples obtained under various conditions, and also on their mechanical features. It is obvious on an example of

SWCNT that the introduction of nanotubes decreases powder shapeability, thereby decreasing composite material density (crude and after sintering). In case of MWCNT, crude density values comparable with powders not containing nanotubes are provided by hydrostatic compression. However, negative effects of nanotubes on density become obvious after sintering. High material densities can be reached only using HIP and through an increase in temperature.

The introduction of nanotubes worsens mechanical properties of obtained materials, regardless of the use of HIP and even after reaching comparable densities. Perhaps, this is due

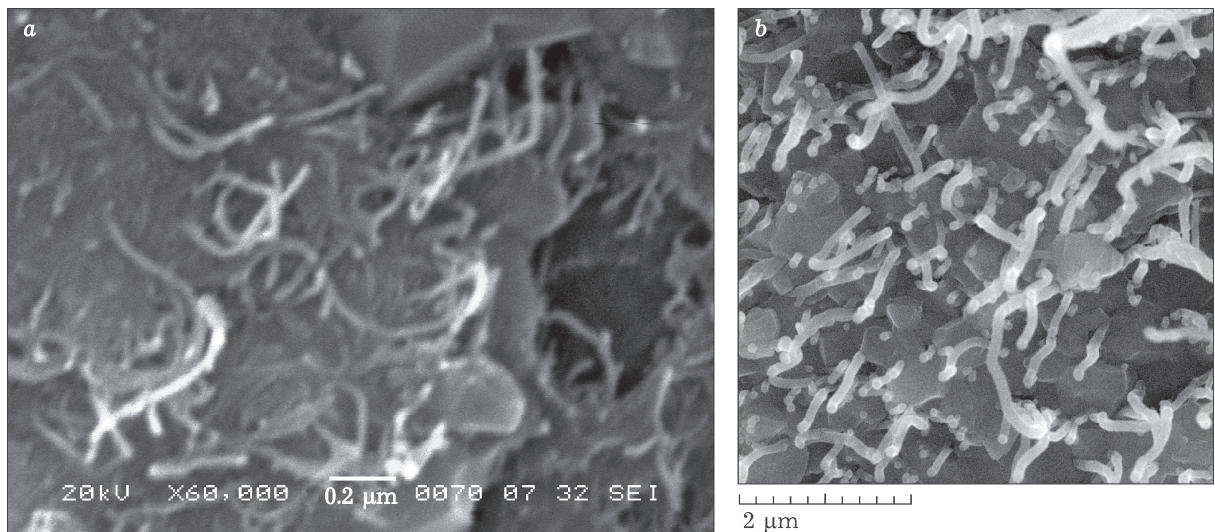


Fig. 5. Electron microscope images of fracture surface of sintered ceramics with $\text{Al}_2\text{O}_3/\text{MWCNT}/$ (a) and $\text{Al}_2\text{O}_3/\text{SWCNT}$ (b).

TABLE 1

Density and hardness of composite materials depending on the composition

MWCNT content, %	Density (ρ_0), g/cm ³				Hardness, GPa
	at sintering temperature, °C				
	0 (initial)	1450	1520	1520 (HIP)	
0.75	2.13	3.40	3.48	–	
0.75*	2.23	3.64	3.76	3.98	23
1.5	2.25	3.53	3.66	3.92	19.8
1.5*	2.26	3.51	3.62	3.97	23.6
2.0	2.07	3.03	3.08	–	
2.0*	2.20	3.17	3.25	–	
0	2.17	3.84	3.86	3.97	26

*Carboxylated nanotubes.

TABLE 2

Density and strength of composite materials depending on the composition

SWCNT content, %	Density (ρ_0), g/cm ³			Bending strength, MPa
	at sintering temperature, °C			
	0 (initial)	1300	1400	
0	2.17	3.65	3.84	380
0.5	2.12	3.56	3.83	255
1	2.05	3.41	3.65	–
3	1.96	2.56	2.89	–

to the fact that it is impossible to provide satisfactory chemical interactions between carbon and alumina.

CONCLUSION

Despite the uniform distribution of single- and multilayer nanotubes in α -Al₂O₃ powders and achieving high densities of sintered composite materials at a relatively low temperature with maintaining nanotubes in the matrix, there is no improvement of the mechanical properties, such as hardness and bending strength. Apparently, this is due to the fact that it is impossible to provide a qualitative interface between the carbon phases and alumina.

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