

NOVEL METAL MATRIX/CARBON COMPOSITES FOR AIRSPACE APPLICATIONS

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Abstract

Carbon nanotubes (CNTs), nanofibers (CNFs) and graphene are promising components for next-generation high-performance structural and multifunctional composite materials. One of the largest obstacles to creating strong, electrically or thermally conductive CNT/CNF or graphene composites is the difficulty of achieving a good dispersion of the carbon nanomaterials in a matrix. Typically, time-consuming steps of carbon nanomaterial purification, ultrasound treatment and functionalization are required. We utilized a novel approach to fabricate composite materials by growing CNTs/CNFs directly on the surface of matrix particles. As the precursor matrix and fillers we utilized metallic copper and aluminum powders. Carbon nanomaterials were successfully grown on these materials. Investigations of the physical properties of the composite materials based on these carbon-modified particles revealed enhanced mechanical and electrical properties.

1 Introduction

Metal matrix composites (MMCs) possess high-temperature capability, high thermal conductivity, low thermal expansion coefficient, and high specific stiffness and strength [1]. These unique physical properties generated vast optimism for the utilization of MMCs in critical space system applications in the late 1980s. Discontinuously reinforced MMCs such as graphite/aluminum, magnesium and copper-based composites were developed both for aerospace and commercial applications [2].

Recently discovered carbon nanostructures such as carbon nanofibers (CNFs), nanotubes (CNTs) and graphene are promising components for next-generation high-performance structural and multifunctional composite materials. One of the largest obstacles to create strong, electrically or thermally conductive CNT/CNF or graphene composites is the difficulty of getting a good dispersion of the carbon nanomaterials in a matrix. Typically, time-consuming steps of the carbon nanomaterial purification, ultrasound treatment and functionalization are required.

Recently, we have proposed a novel approach to create well-dispersed carbon nanomaterials in the matrix by their directly growth on the surface of matrix particles without any additional catalyst [3,4] (Fig.1). This allowed us to produce MMCs without having to resort additional catalyst preparation and multistep processes of CNT/CNF purification, ultrasonication and functionalization for their homogeneous introduction in the metal matrix. The synthesis of CNFs on the surface of metal powder was carried out in a simple one-step chemical vapour deposition (CVD) process.

Here, we utilized this approach to fabricate composite materials on the basis of aluminum, and copper matrix. In this paper we summarize our knowledge and also present new results on the preparation of a good dispersion of CNTs, CNFs and graphene in a matrix, with the intention of improving the mechanical or electrical properties of carbon-based composite nanomaterials.

2 Experimental

For the experiments, copper metal powder with purity of 99% having an average particles size of 5-10 μm and the sprayed aluminum powder with the particle size below 63 μm and purity 99.5 wt.% were used. Copper powder was purchased from Goodfellow. The main admixtures in aluminum powders were silicon,

iron and copper, the content of which did not exceed 0.4, 0.35 and 0.02 wt.%, respectively.

The main conception of method presented in the fig.1. At the first step we had synthesized carbon nanostructures at the surface of micron size metal powder by chemical vapor deposition (CVD) process, and at the second step the samples was compacted by powder metallurgy methods.

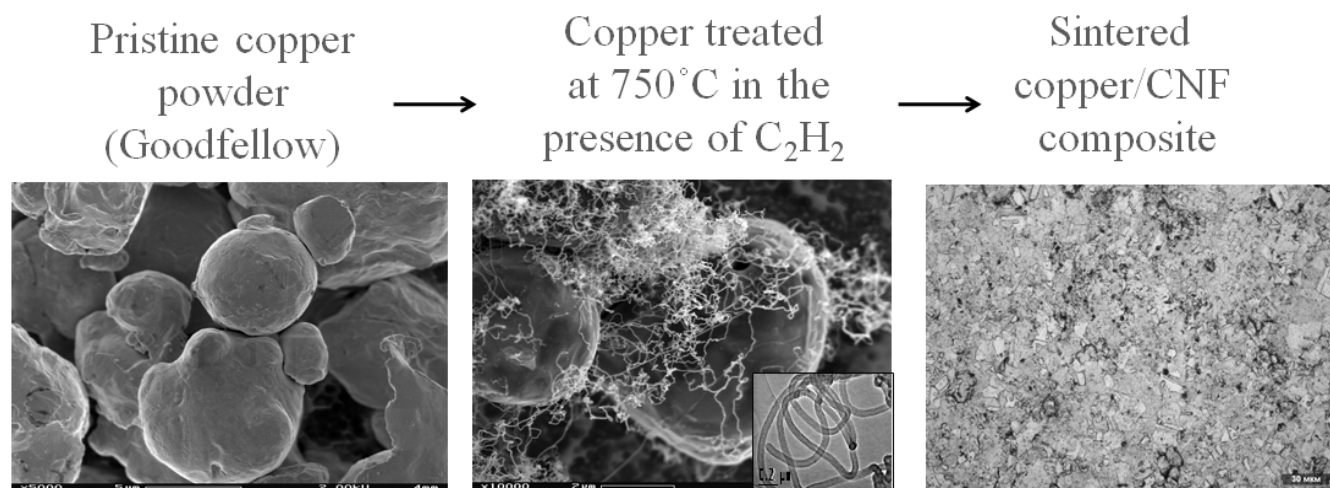


Fig.1. General concept demonstrating our approach to create MMC with enhanced mechanical and electrical properties on the bases of CNFs and copper particles.

For synthesis on the surface of copper particles by CVD, we used an experimental set-up described elsewhere [5]. It consisted of a horizontal quartz tube heated in a resistive furnace in the temperature range from 700 to 940 °C. For the synthesis either 30 cm³/min of C₂H₂ together with 260 cm³/min of H₂ (for CNF growth) or 120 cm³/min of C₂H₄ together with 240 cm³/min of H₂ (for graphene growth) were introduced into the reactor. For the synthesis of the carbon materials, the reactor was heated to the desired temperature in inert gas (N₂ or Ar) atmosphere (100 cm³/min). Then, a ceramic crucible with the copper powder (~2 g) was placed in the middle of the reactor. After 5 min N₂ was replaced by 240 cm³ min⁻¹ H₂ flow for 5 min in order to reduce the surface copper oxide. Then the carbon source was introduced together with H₂. After 10–20 min, the mixture of C₂H₄ and N₂ was switched to pure N₂ and the crucible was moved inside the quartz tube outside the hot zone to cool down to room temperature.

Aluminum - carbon nanofibers composite powders had been produced by gas phase

synthesis of nanofibers on the surface of the matrix of metal particles by adding nickel catalyst. The influence of Ni catalyst content on morphology of composite particles described in [6] in details. Uniform distribution of catalytic particles and subsequently CNFs were obtained at the concentration of the nickel of 0.02 wt.%. The nickel source was a Ni(NO₃)₂ 6H₂O salt that has a high solubility in water and decomposes to NiO at a temperature of 300 – 350 °C in air atmosphere. Then the powder was heat treated additionally in a hydrogen atmosphere for complete decomposition of the salt and reduction of nickel.

For aluminum powders the temperature of the CNF synthesis was varied from 500 to 700°C. We use acetylene gas as a carbon source. Synthesis runs in the H₂/C₂H₂ mixture for 5-15 min. The hydrogen-to-acetylene ratio in the gas mixture during the synthesis H₂/C₂H₂ was maintained to be 8.3/1.

At the beginning the composite powders were compacted by uniaxial cold pressing at the pressure of 500-600 MPa in order to make cylindrical samples of 10 mm in diameter and a

height of 4 mm. Then the specimens were compacted to full density by the two methods: (i) hot pressing and (ii) sintering at 600°C in an argon environment.

Hot pressing was carried out on a hydraulic press DA0040 of 1000 ton-force in the pressure chamber of the "truncated hemisphere" at 5 ± 0.5 GPa at variable temperatures. The pellet was placed in a high pressure vessel between two graphite tablets. Heating the high pressure container was performed by passing the alternating electrical current (0.3-0.8 kA) at a voltage of 3-6V in the mode of stabilization of electric power. The accuracy of stabilization of electric power is not less than 5%. The temperature inside the container was determined from the calibration "power - temperature" curve with the accuracy of ± 50 °C.

We studied the structure of the samples by the methods of scanning (SEM, Leo DSM 982 Gemini and JEOL JSM-7500F) and transmission (TEM, Philips CM200 FEG) electron microscopy. The Raman spectra were recorded at room temperature in monochromatic radiation of a YAG laser (532.25 nm, 30 mW). The density of the sintered specimens was determined by hydrostatic weighing.

The measurements of thermal diffusivity (cm^2/s) were carried out on the DXF-200 equipment by TA-Instruments. To create a momentum of temperature on the front side of the sample using the flash of xenon lamp, and the change in temperature on the back side of the sample is fixed by contact thermocouple. For measurements, the flash duration was set to 500 ms. Heat conductivity was calculated by using of measured values of thermal conductivity by equation: $\lambda = \alpha \cdot \rho \cdot c_p$, where, c_p (J/(g*K)) is heat capacity and ρ (g/cm³) is density of sample. Declared by the manufacturer the accuracy of thermal diffusivity, heat capacity, and thermal conductivity measurements is $\pm 2.3\%$, $\pm 4.0\%$ $\pm 5.0\%$ respectively.

3 Results and Discussions

3.1 Synthesis of Composite Powders

As revealed by SEM observation independently on the gas precursor carbon product synthesized at temperature interval left of the maximums was amorphous. SEM images of the copper powder treated at temperatures of 740 and 940 °C in acetylene and ethylene atmosphere correspondingly presented on Fig. 2. As seen from the picture the specimens treated in acetylene revealed abundance of high aspect ratio nanofibers (Fig. 2a), however the particles treated in ethylene don't revealed any fibers, but are covered by a smooth carbon layer.

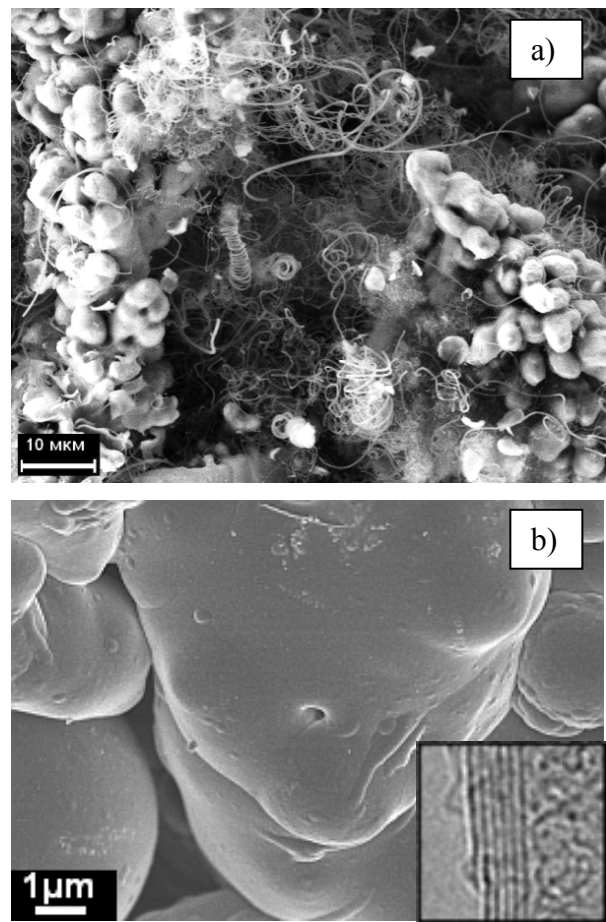


Fig. 2. The copper powder treated in acetylene at temperature of 740 °C (a) and in ethylene at temperature of 890 °C (b).

TEM images of the carbon coatings removed from the copper particles treated in ethylene are presented on inset of figure 2. As was observed by TEM the carbon coatings obtained at temperature of 940 °C contained 8-12 layers of graphene with interplanar distance of 0.373 ± 0.05 nm. At lower temperatures only amorphous carbon was found. In an attempt to decrease the number of the layers,

the duration of the treatment was decreased from 20 to 10 min. However, neither the weight of the sample, nor the number of the layers changed with shorter growth time. Therefore, for the mechanical tests we utilized the samples prepared at 10 min growth time.

Thus utilizing copper particles and varying the carbon source from C_2H_2 to C_2H_4 , we were able to alter the carbon product from nanofibers to few-layered graphene on the surface of micron-sized copper particles.

A method for making an “aluminum – carbon nanofibers” composite material is presented in [6]. To obtain good distribution of carbon nanostructures in the matrix we deposited a nickel catalyst onto the surface of the aluminum particles. After Ni catalyst deposition carbon nanostructures were synthesized at a temperature of 550°C for 5 – 15 min. Carbon fibers cover the matrix particles virtually fully and the diameter of the fibers is 20 – 40 nm as shown in the Fig.3. The mass grows primarily due to the increase in the length of the fibers. The maximum weight increase is about 15 wt.%.

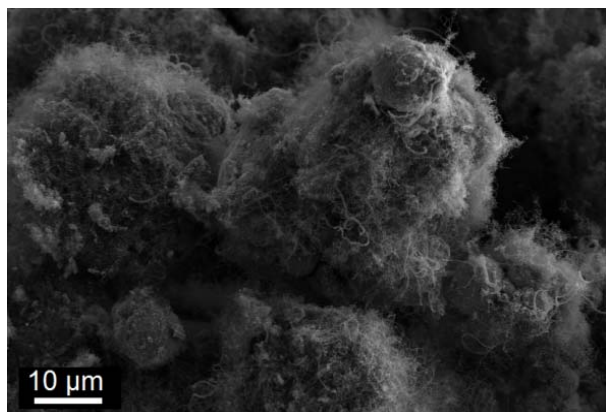


Fig. 3. SEM image of CNFs synthesized during 15 min at 550 °C at the Ni concentration of 0.035%.

3.2 Compact samples preparation

To evaluated their mechanical and physical properties the Cu-CNFs powders were compacted through cold isostatic pressing with subsequent sintering; however, the syntheses of the graphene proceeds at temperatures about 940 °C, when significant sintering of the copper powder occurs, that makes impossible to apply the same

technological route, so the partly sintered Cu-graphene powders were subjected to cold rolling.

The microstructures of the samples after compacting process were analyzed; their images are presented in Fig. 4. Cu-CNF composite contains finer grains (around 4 μm) with carbon homogeneously dispersed between them (Fig. 4(a)). Apparently a good dispersion of CNFs in the matrix prevented the grain growth during sintering.

Experiments on fabrication of aluminum compact materials containing 1 wt.% carbon nanostructures by cold pressing and sintering shows that the density of the sintered specimens exceeds 98% of the theoretical value. As compared to the control specimens from aluminum powder with catalyst, the hardness increases by 20% at satisfactory ductility. When the specimens obtained are deformed by rolling with reduction of up to 40% at room temperature, visible defects are absent.

Hot pressing of samples was run at the temperatures of 480, 720, and 980°C and the pressure of 5 GPa. The pressure dependence of aluminum melting point is described by equation [7]: $T_{melt}(p) = T_{melt}(p_0) + dT/dp$, where $T_{melt}(p_0) = 660$ °C, and $dT/dp = 64.1$ K/GPa. $dT/dP = 6.41 \cdot 10^{-2}$ [K/MPa], i.e. at the 5 GPa pressure the melting point of aluminum is about ~980°C. Structure and properties of hot pressed samples was study in detail in [8]. The microstructure forms equiaxed, close to hexagonal grains of aluminum, separated by carbon layers with thickness less than 1 μm and in all cases showed absence of porosity, all the samples had a density close to theoretical value.

Fig. 4(b) shows micrographs of a typical microstructure of the samples hot pressed at 720°C. Study of the structure in all cases showed absence of porosity, all the samples had a density close to theoretical value. The microstructure forms equiaxed, close to hexagonal grains of aluminum, separated by carbon layers with thickness less than 1 μm.

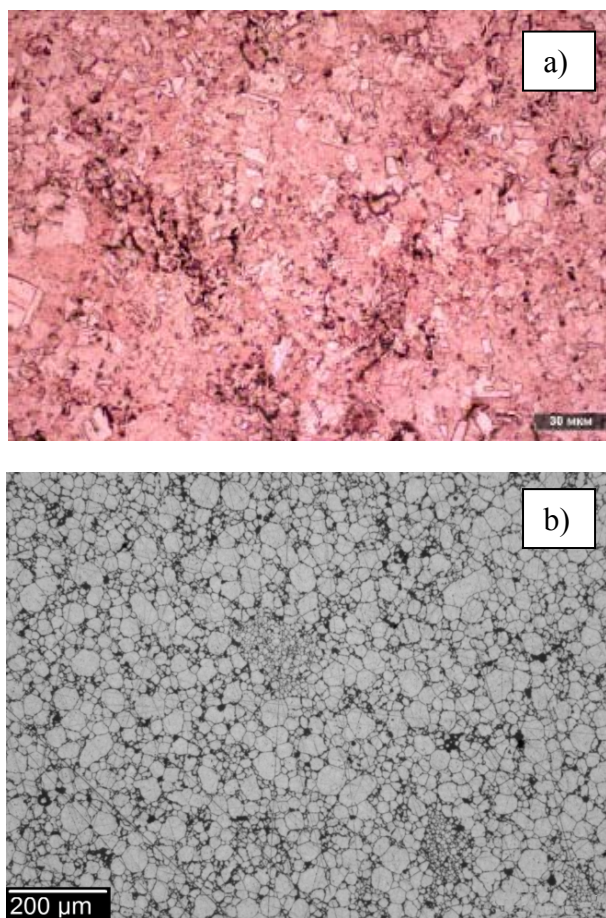


Fig. 4. Typical microstructures of Cu-CNF (a) and Al-CNF composites.

Energy-dispersive analysis showed the absence of carbon as well as copper and iron inside the aluminum grains. X-ray photoelectron spectroscopy (XPS) study shows the presence of oxygen, aluminum and carbon. Al is in the form of metallic state and aluminum oxide Al_2O_3 . Oxygen preferably presence in the form of alumina. It was found the presence of aluminium carbide Al_4C_3 in the hot pressed samples at the temperatures 720 and 980°C. XRD analysis

shows only peaks belong to aluminum in the initial powder and samples compacted at 480 и 720 °C, however, the crystalline alpha alumina appears at the 980°C, 5GPa. There are no any other crystalline phases such as carbides or oxides were found.

3.3 Physical and mechanical properties

Comparative analysis of the hardness of different Cu/C composite materials was performed (Table 1). Cu/graphene composite showed a 39% increase in hardness compared to pure copper, while 10% and 70% improvements were found for Cu/graphene and Cu/CNFs composites, respectively [4].

As can be seen, the hardness of the composites correlates very well with the grain size: the smaller the size, the greater the hardness. As can be seen in Fig. 9, Cu/CNF composite has the narrowest grain size distribution with the smallest mean size of around 4 μm , which means it possesses the most homogeneous and finest structure. Most likely a good dispersion of CNFs in the matrix results in filling the interparticle pores, preventing grain growth during the sintering process. The reason for hardening may be also not just the grain size, but good dispersion strengthening the copper matrix with CNFs. In the case of higher CNF concentrations one can even see carbon inclusions inside the grains.

Thus, on the basis of the mechanical test results and sample observation we can propose that the effect on the mechanical properties of

Table 1. Properties of copper – carbon composite materials.

Material	Relative density, %	Hardness, HB	Electric resistivity $\Omega \cdot m$ (not more)	Elongation, %
Cu	98	35	$1,8 \cdot 10^{-8}$	55,0
1% CNF	98,5	60	$1,9 \cdot 10^{-8}$	39,0
3% CNF	98	60	$1,9 \cdot 10^{-8}$	38,6
5 % CNF	97	52	$2,2 \cdot 10^{-8}$	31,4
3% graphene	96	48	$2,0 \cdot 10^{-8}$	25,2

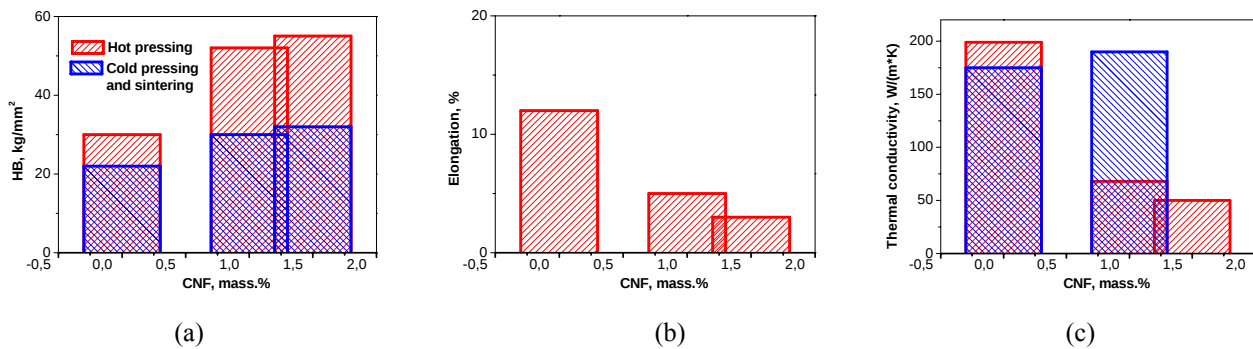


Fig. 5. (a) Mechanical properties and electrical of aluminum/CNF composites: hardness (a), elongation at the bending test (b), and thermal conductivity of composite materials. Hot pressing temperature is of 720°C and pressure 5 GPa.

the composite materials can be explained not by the reinforcement by carbon nanomaterials, but by the suppression of grain growth during the sintering process. Mainly the improvement in the mechanical properties of the C/Cu-based composite materials is attributed the crystallite or grain formation of the matrix material.

We have also carried out a comparative analysis with Al/CNF composites prepared by cold pressing and sintering and Al/CNF composites prepared by hot pressing (Fig. 5). As expected, any CNF additions to aluminum led to hardening of the composite. However, Al/CNF composite prepared by hot pressing showed about 80% increase in the hardness compared with samples prepared by cold pressing and sintering. There is significant increase in hardness at the CNF content up to 1%, which continuously increases up to 1.5%. The hardness of samples contained 2% CNF haven't any changes and even shows the tendency to decrease.

The elongation of hot pressed samples with 1%CNF compacted at the temperature of 720°C is about 5% at the hardness of 54HB. At the same conditions the samples of pure aluminum have elongation of 12%, that is much smaller as compare with composite samples made by cold pressing and sintering.

The thermal conductivity of compact Al of high purity, which is 237 W/(m·K) at 300 K [7]. The values of composites conductivity are in the interval 43-75 W/(m·K). It is much smaller as compare with the samples prepared by cold pressing and sintering (150-190 W/(m·K)). Low thermal conductivity of aluminum/CNF composites, associated with the presence of

thermal barrier at the filler - matrix interface that is also noted in [9]. Increasing the thermal resistance provided by boundaries forming carbide and/or oxide as the thermal conductivity of such compounds significantly lower the conductivity of pure metal and is in the range of 10 to 40 W / (m K) [10] for carbides, and is about 30 W / (m K) for alumina [7].

Finally we should conclude that carbon nanomaterials were successfully grown on the surface of copper and aluminum metallic powders. Investigations of the physical properties of the composite materials based on these carbon-modified particles revealed enhanced mechanical and electrical properties and strongly depend on technological parameters. However, this study shows the way to solve one of the largest problem to creating strong, electrically or thermally conductive CNT/CNF or graphene composites: the difficulty of achieving a good dispersion of the carbon nanomaterials in a metal matrix.

4 Conclusions

We have proposed a novel approach to create well dispersed carbon nanomaterials by directly growing these on the surface of matrix particles, resulting in further improvements of the mechanical and electrical properties of the composite materials. Utilizing copper particles and varying the carbon source from C₂H₂ to C₂H₄, we were able to alter the carbon product from nanofibers to few-layered graphene on the surface of micron-sized copper particles. Comparative analysis of the hardness of different Cu/C composite materials was performed. Cu/graphene

and Cu/CNFs composites showed a 39% and 70% 10% increase in hardness compared to pure copper, while specific elongation is about 20%.

We have shown the possibility of fabrication of a composite “aluminum – carbon nanofibers” material by gas phase synthesis in an acetylene-hydrogen mixture on the surface of micron particles of aluminum containing up to 15 wt.% carbon nanofibers. In the method used we deposited a nickel catalyst onto the surface of an aluminum powder from an aqueous solution of nickel nitrate. Uniform distribution of carbon nanofibers was obtained at a minimum content of nickel catalyst equal to 0.035 wt.%.

An aluminum composite material prepared using 1 wt.% CNFs obtained by uniaxial cold pressing and sintering showed 30% increase in the hardness compared to pure aluminum, whereas the composites prepared by hot pressing showed 80% increase in the hardness. Composite materials have satisfactory ductility of about 5% at the compacting temperature of 720°C. Thus, the aluminum based material reinforced with carbon nanostructures should be appropriate for creating high-strength and light compacts for aerospace and automotive applications and power engineering.

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