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Research of the Interaction Energy of Carbon Nanotubes in the Agglomeration Process

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Abstract
This paper presents the calculations of the influence of the spatial arrangement of the carbon nanostructured filler on the value of the agglomeration energy. The values of the energy of van der Waals interaction for parallel and cross arrangement of CNTs have been determined. Analysis the values of the energy of van der Waals interaction conclude that only at sufficiently energy one can achieve complete separation of CNTs.

Keywords: carbon nanotubes, interaction energy, agglomeration, metal matrix, composite materials.

1. Introduction

Modern powder composites with a metal matrix have a low coefficient of friction and high wear resistance [1]. However, the strength of these composite materials is lower than that of cast metals [2]. In addition, these composites are incombustible and resistant to most radiation, have high electrical and thermal conductivity [3]. Studies of metal-matrix composites have shown the possibility of their application in the aerospace, automotive and instrument-making industries.

Continuous and discontinuous fibers, whiskers, and solid dispersed particles are used as fillers for metal-matrix composites. Typically, fillers for composite materials are a ceramic phase in the form of oxides, carbides, and nitrides [4].

Both metals and alloys are used as matrices of composite materials. For example, composites based on an aluminum matrix are widely used in the production of parts for fastening systems, pistons and brake discs [5]. Matrices based on titanium and its alloys have high strength characteristics [6]. Magnesium is a light metal, but it is prone to atmospheric corrosion, which makes it unsuitable for many applications [7]. Beryllium is also one of the lightest structural metals. However, it is extremely fragile. Nickel, cobalt and their alloys tend to oxidize reinforcing fibers at elevated temperatures [8].

Copper is one of the common metals for matrices of composites. Copper possesses ductility, high electrically conductive and thermotechnical characteristics, as well as resistance to corrosion. In many cases, the use of copper as a matrix of a composite material is justified [9, 10].

In recent years, there has been a tendency to reduce the size of dispersed fillers of metal-matrix composite materials. Currently, there is considerable interest in composites with nanoscale particles. Carbon nanotubes (CNTs) have high strength and tribotechnical characteristics and

are used as fillers for metal matrix composite materials [11, 12]. CNTs range in length from hundreds of nanometers to tens of microns and often contain various defects.

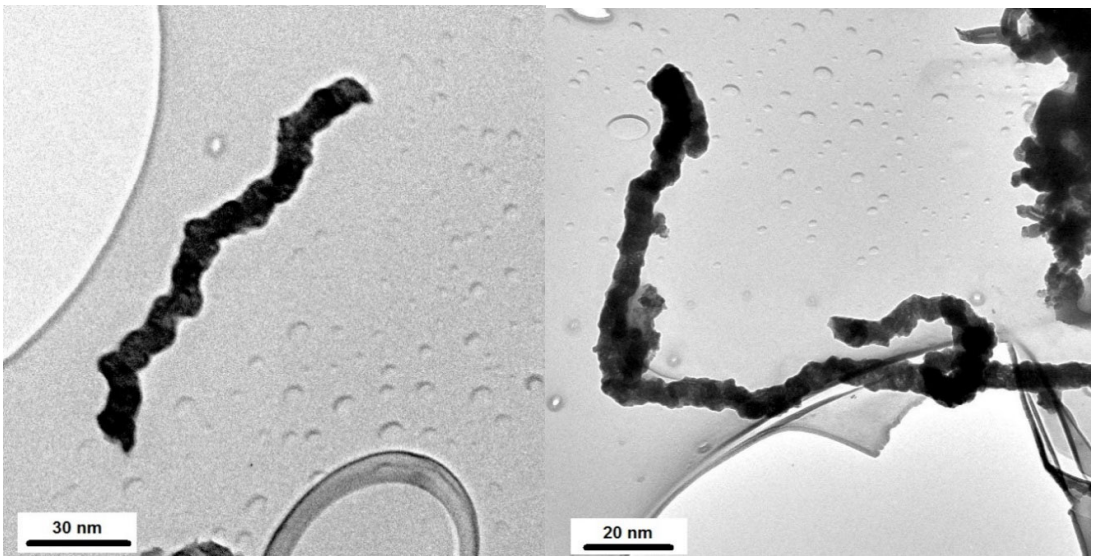

Figure 1. Size and shape of CNT

In many works [13 – 17] it is shown that the introduction of CNTs into a metal matrix significantly improves the mechanical, tribotechnical and heat-conducting properties of composite materials based on a metal matrix.

However, the formation of a homogeneous structure of metal-matrix composites is difficult, since individual CNTs under the action of van der Waals forces tend to combine into agglomerates [18]. A typical example of finding CNTs in an agglomerated form in a powder composition is shown on Figure 2.

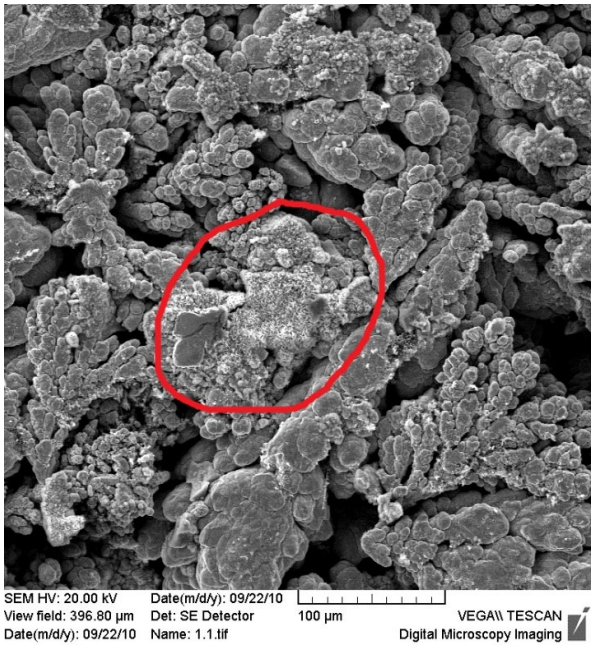

Figure 2. The structure of the metal matrix composition "copper – CNT" with CNT agglomerate

Controlling the structure of composite materials with micro- and nanoscale components is a problematic issue. Difficulties are associated with obtaining a uniform distribution of CNTs in a metal matrix. The distribution of CNTs in the matrix is a key point in controlling the structure formation of nanostructured composites [19].

Obtaining composite materials of this class requires the use of technological methods of preliminary processing [20]. In this case, even a small amount of well-dispersed CNTs can significantly improve the properties of composite materials [21].

For the destruction of CNT agglomerates, their distribution in the metal matrix, it is advisable to use mechanical activation [22]. The process of distribution of a nanosized filler in a metal matrix can be represented as the supply of mechanical energy to the initial components of the powder system to separate micro-sized agglomerates. In this case, the binding energy of nanoparticles of agglomerates is a counteracting factor that hinders the separation of nanosized components.

Taking into account the above, it is possible to establish criteria for the effective separation of agglomerates in the process of mixing nano- and micro-sized starting components of composite materials. First, for the destruction of agglomerates, the supplied energy must exceed the binding energy of the CNT. Second, in order to preserve the physical and mechanical characteristics of individual CNTs, the amount of supplied energy should not exceed the destruction energy of a single CNT. Consequently, the optimal method for separating agglomerates of nanosized filler should provide a lower limit on the amount of input energy sufficient to destroy the bond of agglomerates and the upper limit of energy is insufficient to destroy individual CNTs.

It is necessary to evaluate the forces that bind CNTs into agglomerates. The shape and geometric dimensions of CNTs differ depending on the methods of their synthesis; however, the forces of interaction between pairs of nanotubes can be estimated using theoretical models, which will be illustrated below.

The purpose of the work was to study the value of the interaction energy of carbon nanotubes in the process of agglomeration.

2. Materials, research methods and models.

In this work, the calculations were performed for multilayer CNTs with an outer diameter of 20 nm and a length of 900 nm. For example, a samples of a powder metal matrix nanostructured material “copper – CNT” with a CNT content of 0,07 wt. % with overall dimensions 15×15×15 mm.

The analysis of the van der Waals interaction of two CNTs was performed using the Hamaker constant [23]. The interaction energy was determined by modeling each CNT as a mesoscale rod continuum [24]. It was experimentally established that for the van der Waals interaction between the outer wall of a multilayer CNT and a metal surface in vacuum, the Hamaker constant is $A_H = 60\times10^{-20}$ J [25]. The Hamaker constant makes it possible to determine the energy of van der Waals interaction between a pair of parallel CNTs. The solution to this problem is similar to the solution, which describes the energy of van der Waals interaction between two parallel mesoscopic cylinders of length l and diameter d, separated by a gap H (Figure 3, a) [26]:

$$E_{//} \approx \frac{A_H}{24} \cdot l \cdot d^{\frac{1}{2}} \cdot H^{-\frac{3}{2}} \text{ at } H \geq H_c \quad (1)$$

where A_H is the Hamaker constant, l – CNT length, d – CNT diameter, H – distance between interacting CNTs, H_c – distance between graphene layers of multilayer CNT (0,34 nm).

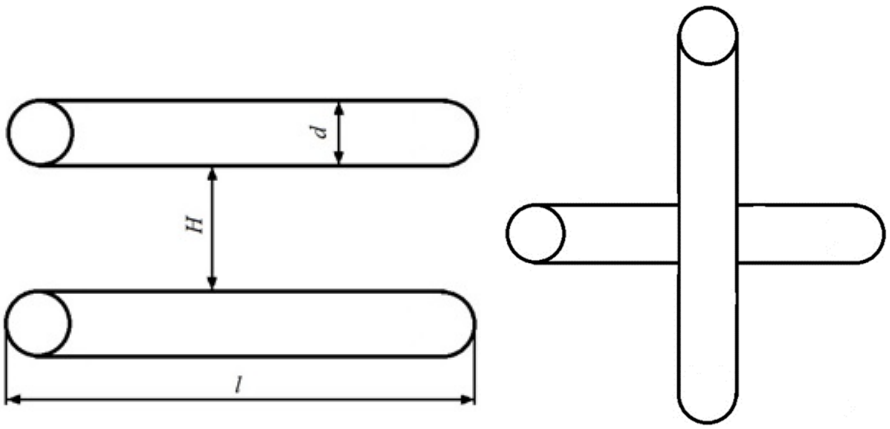

Figure 3. Scheme of the spatial relationship of CNTs during interaction: parallel (a) and cross (b)

The interaction energy of two CNTs can be modeled by two perpendicularly crossed rods of diameter *d* located at a distance *H* (Figure 3, b) [26]:

$$E_+ \approx \frac{A_H}{12} \cdot \frac{d}{H} \quad \text{at } H < d \tag{2}$$

To estimate the amount of energy for destruction of CNT agglomerates and to understand the processes of structure formation, it is necessary to carry out calculations. Let's calculate a cubic sample of a composite material “copper – CNT” with a long side of 15 mm. The volume of this sample is calculated by the formula:

$$V_s = a \cdot b \cdot h \tag{3}$$

where *a, b, h* is respectively the length, width and height of the sample.

The density of the sample:

$$\rho_s = \rho_{Cu} \cdot f_{Cu} + \rho_{CNT} \cdot f_{CNT} + \rho_{por} \cdot f_{por} \tag{4}$$

where f_{Cu}, f_{CNT}, f_{por} are the volumetric content of copper, CNTs, pores, respectively; $\rho_{Cu}, \rho_{CNT}, \rho_{por}$ are the density of copper, CNT and pore, respectively.

Sample mass:

$$m_s = \rho_s \cdot V_s \tag{5}$$

Using the mass of the sample, we determine the mass of the carbon nanostructured filler:

$$m_{CNT} = m_s \cdot \frac{\gamma}{100}$$

where γ is the mass content of CNTs in the composite material.

The volume of CNTs in the sample:

$$V_{CNT} = \frac{m_{CNT}}{\rho_{CNT}} \quad (6)$$

Volume of one CNT:

$$V_{1CNT} = \frac{\pi \cdot d^2}{4} l \quad (7)$$

where d_{CNT}, l are the diameter and length of the CNT, respectively.

The number of CNTs in the sample:

$$n_{CNT} = \frac{V_{CNT}}{V_{1CNT}} \quad (8)$$

Energy of van der Waals interaction of carbon nanosized filler in the sample:

- for parallel arrangement

$$E_p = 0{,}5 n_{CNT} \cdot E_{//}$$

- for cross arrangement

$$E_c = 0{,}5 n_{CNT} \cdot E_{+}$$

Total interaction energy is

$$E = E_p + E_c$$

3. Results and discussion

The distribution of CNTs in the metal matrix determines the properties of the composite and is a significant problem. The results of the calculations performed to determine the energy of the van der Waals interaction of CNTs are shown in Figures 4 and 5. The dependences of the energy of van der Waals interaction for parallel and crossed arrangement of two CNTs are shown in Figure 4. The total interaction energy is shown in Figure 5. At the same time, it is assumed that all CNTs of the sample are in an agglomerated form and interact with each other.

The values of the energy of van der Waals interaction in the case of parallel arrangement of CNTs significantly exceed the values of the energy in the case of crossing arrangement, which is explained by the considerable length of the interaction (Figure 4). For example, at a distance of 1 nm, the energy of van der Waals interaction of two CNTs in a parallel arrangement is $\approx 10^{-16}$ J, and when crossed $\approx 10^{-18}$ J.

The calculated values obtained correlate with the literature data. In [27], the calculation of the interaction energy of two parallel CNTs is presented. In this work was shown that the cohesive interaction energy per unit length between two CNTs is approximately 0,095 eV/Å ($1{,}56 \times 10^{-20}$ J/Å).

In works [18, 26], for crossing CNTs 10 nm in diameter located at a distance of 0,34 nm, the calculated values of the interaction energy equal to 10 eV ($1{,}6 \times 10^{-18}$ J) and 15 eV ($2{,}4 \times 10^{-18}$ J). These values, calculated on the basis of the surface integral of graphene layers, are somewhat lower, but comparable with the values obtained in this work. The value of the van der Waals energy that binds CNTs into agglomerates, presented in [28], is ~ 500 eV/μm (8×10^{-17} J/μm).

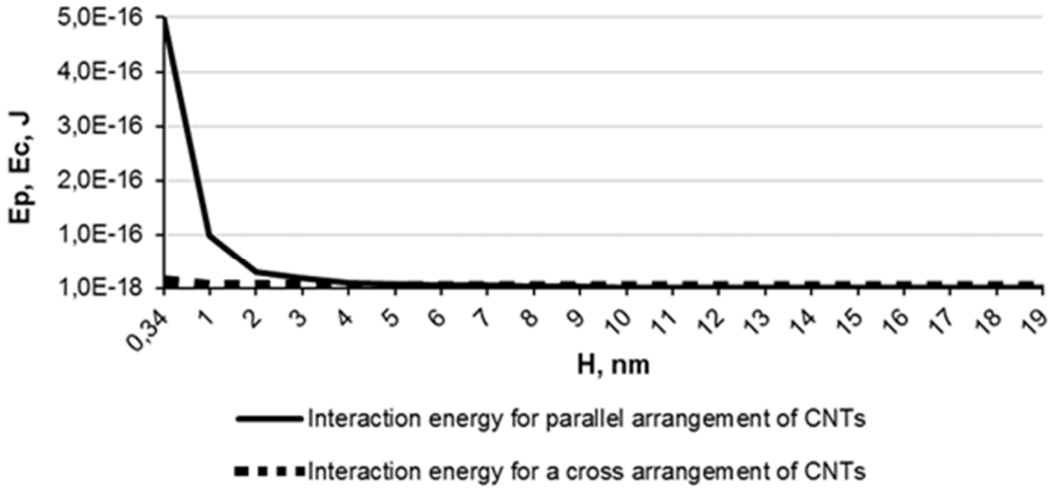

Figure 4. Energy of van der Waals interaction for parallel and cross arrangement of CNTs

The analysis of the calculated values showed that an energy of 0,082 J is sufficient to separate the agglomerated CNTs located in the test sample (Figure 5).

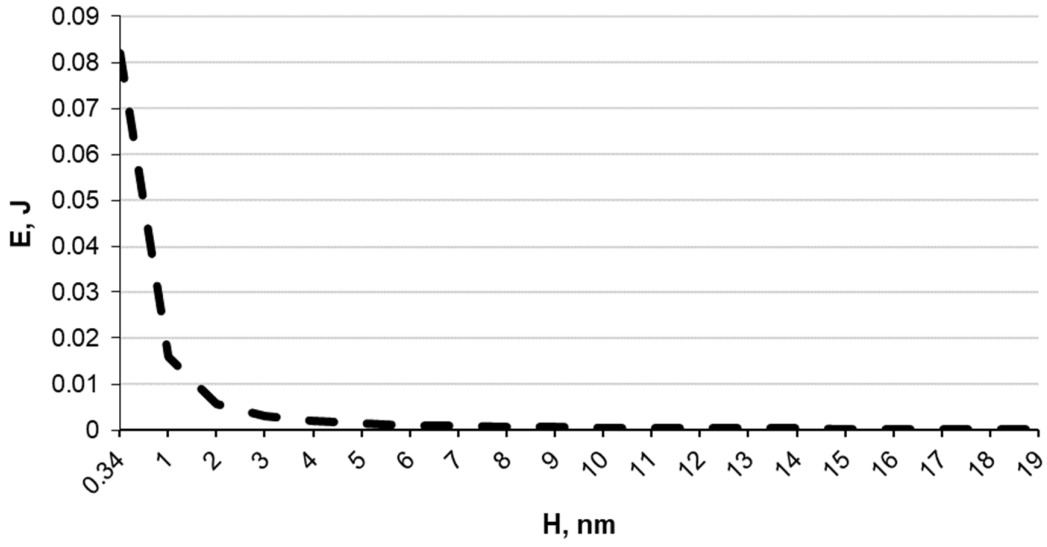

Figure 5. The total energy of van der Waals interaction of CNTs in the agglomerate

4. Conclusions

This paper shows the influence of the spatial arrangement of the carbon nanostructured filler on the value of the agglomeration energy. Calculations have been made for parallel and cross arrangement CNTs. The values of the energy of van der Waals interaction for parallel and cross arrangement of CNTs have been determined. The values of the interaction energy for parallel arrangement CNTs exceed the energy values for the cross arrangement of CNTs. This is due to

the considerable length of the interaction. An increase of the distance between interacting CNTs significantly reduces the interaction energy. Analysis the values of the energy of van der Waals interaction suggest that only at sufficiently energy one can achieve complete separation of CNTs. The considerable energy input also induces unwanted CNTs breakage.

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