INVESTIGATION OF STRUCTURE AND PROPERTIES OF COMPOSITE MATERIALS BASED ON COPPER – CARBON NANOPARTICLES POWDER SYSTEMS FORMED BY ELECTROCONTACT SINTERING

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Abstract: Investigation results of physico-mechanical properties and structure of composite powder materials based on copper matrix and carbon nanoparticles formed by the method of electrocontact sintering are presented. The investigations by the methods of scanning electron microscopy show the influence of preliminary mechanical activation of the powder system on distribution of carbon nanoparticles in the metal matrix. Mechanical activation ensures mechanical bonding of nanoparticles on the surface of metal particles thus giving a possibility for manufacture of a composite with high physico-mechanical properties.

KEYWORDS: POWDER METALLURGY, ELECTROCONTACT SINTERING, PHYSICO-MECHANICAL PROPERTIES, CARBON NANOPARTICLES, COMPOSITE POWDER MATERIALS, TRIBOENGINEERING CHARACTERISTICS, MECHANICAL ACTIVATION.

1. Introduction

Modern level of competitive machinery implies the development and application of novel composite materials that display high strength properties and wear resistance [1, 2]. Known in the art composites on the base of a metal matrix with dispersed carbides, oxides as well as diamond and graphite particles are used in manufacture of triboengineering components [3-5]. Micron-sized particles, dispersed in such materials, however, are known to be imperfect fillers. Nanoparticles are more appropriate in this respect [6]. The powder systems containing nanodispersed particles belong to a new generation of composite materials.

One of the ways of obtaining antifrictional composites is impregnation of carbon nanostructures possessing high triboengineering and physico-mechanical characteristics into the powder matrix [7-9]. The use of macrolevel carbon nanotubes (CNT) and onion carbon nanostructures (OCN) as antifrictional and reinforcing fillers has promoted further development of composite materials operating in dry friction joints [10]. Such properties of CNT like high specific surface, the dimensions commensurable with the forces of intermolecular interactions, along with high strength, thermal and electric conductivity lie in the base of their engineering applications [11]. It should be noted that the works on developing new materials incorporating different nanostructures are at the height of activities at present [12].

Carbon nanostructures tend to agglomerate in a free state [13, 14], whereas the majority of metals used in industry enter into interactions with carbon under high temperatures forming new chemical compounds called carbides [15]. That is why, to reach a homogeneous distribution of carbon nanostructures in a molten metal matrix when new chemical compounds between carbon and metals are being formed presents certain difficulties. In this connection, the methods of powder metallurgy show promise as economically sound, advanced procedures for obtaining composite materials based on the systems of metal-carbon nanostructures. The process of electrocontact sintering of the initial compacted powder blanks lasting from a second till a few minutes seems to be advantageous for these purposes. In this case, the composite material is manufactured in the conditions characterized by short-term physical processes, high-rate internal heating and a sharp temperature gradient, under which the hereditary structure of the material is preserved. Powder particles tend to bond via the diffusion-free setting and welding (in the solid, solid-liquid and liquid phases) based on diffusion processes. The share of participation of these processes depends on the heating temperature, pressing force, time of current flow and other technological parameters [16].

One more important problem in manufacture of composite materials based on a metal matrix and carbon nanostructures is the way of impregnating nanosize components into the system having a microsized matrix, as well as wetting of the nanostructures by the molten matrix metal. The surface of carbon nanostructures is perfectly wetted by the matrix metal whose free surface energy is within 100-200 mN/m [17]. The problem of wetting carbon nanostructures with the surface energy surpassing 200 mN/m was solved in 1996 by oxidation of carbon nanostructures [18]. Notice, that chemical surface functionalization of carbon nanostructures affects inevitably their mechanical properties. This effect is, however, limited by degradation of all unique properties of carbon nanostructures by 15-20%.

In spite of a great number of publications, the questions of combining microsize and nanodispersed powder components have not lost their actuality till now. The problem consists in obtaining a powder system having a uniform distribution of carbon nanostructures (initially present in the form of agglomerates) over the whole volume of the matrix and their strong bonding inside the metallic matrix of the composite material.

2. Mechanical activation of powder systems

Mechanical activation of the initial components of powder systems is believed to be a promising method used in powder metallurgy to control structure formation processes in composite materials. Particularly, to hamper agglomeration of carbon nanostructures [18], to ensure their uniform distribution in the matrix, and raise modifying activity of metals the initial components are subjected to mechanical activation in activators of various configurations.

The mechanical activation leads to enlarged specific area of metal particles, modification of their surface structure, and plastic strains that result in structural defects enabling to improve interaction between the components. In combination, these processes alter the free surface energy of the substance, decreasing thereby the energy potential of physico-mechanical processes [19]. The intensive plastic strain leads to significant structural and phase transformations in the material. One of the commonly encountered outcomes of the intensive plastic strain is the shift of the phase transition temperature limits accompanied by a reduced time of the following thermal treatment, improved strength and service characteristics of the final products under lower energy consumption.

The mechanical activation takes place only if the rate of defect accumulation in the particles surpasses that of their disappearance [20]. This can be realized in so-called energy-intensive equipment, namely, centrifugal, planetary and jet-type mills, disintegrators and other machinery where high frequency is combined with high mechanical forces.

The efficiency of mechanical activation depends on the amount of the energy accumulated by the material treated. This parameter depends on several factors, among which are the activator type, mechanoactivation medium, size to mass ratio of the working bodies and particles of the treated material. The desired
effect from mechanoactivation can be attained, as a rule, through a laborious matching of treatment conditions, i.e. empirically. These conditions are very specific for any complex system and its components. It is important to define the regularities of variations in energy properties of complex systems and their components as a function of mechanoactivation conditions. As a result, it will be possible to make a preliminary estimate of reactivity of the materials and to put forward recommendations on most efficient conditions for their processing.

It has to be noted that the powder material activated by a free-impacting method is characterized by a fragmentary particle shape with a large number of cleavage facets, cracks and other defects positively effecting bonding strength between carbon nanostructures of highly developed contact surface and metal particles. This bonding proceeds the faster and more completely the larger the surface of the substance participating in the process.

Mechanical activation of the metal matrix components of the composite enables not only to enlarge its specific surface and obtain a required granulometric composition, but also to improve the particle surface quality by removing and breaking surface oxide films [21]. Notice that, prolonged activation of one and the same powder charge promotes the removal of impurity films and imparts high degree of homogeneity. The activation decreases the temperature of sintering, increases its velocity and reduces time.

3. Investigation methods and materials used

The ingredients of the powder system used for obtaining composite materials were copper powder PMS-V (State Standard GOST 4960-75) 50-100 μm in size and a combined carbon nanostructural filler (CCNF). CCNF is a bicomponent composition consisting of 20% CNT (Fig. 1a) and 80% of OCN (Fig. 1b) obtained after benzene pyrolysis. CCNF content in the powder systems varied within 0.01 till 0.1 mass% with a stage by stage increase from 0.01 till its maximal content.

The process of mechanoactivation was carried out using a developed pilot mechanical activator. Its distinguishing feature is an intensive vibration effect going hand in hand with impacting and rolling processes.

The structure and phase composition of the activated powder systems were studied by a scanning electron microscopy using standard procedures. Their hardness was measured on a Brinell’s machine (GOST 9012–59). The compressive strength limit was found on a universal testing machine of the type TsD-20 (GOST 25.602-80). The porosity of the sintered composite materials was determined by the method of hydrostatic weighing following GOST 18898-73 that specifies the methods for determining density and porosity of compacted and sintered components in powder metallurgy.

Triboengineering tests with a friction geometry shaft-partial insert have been carried out on a friction machine SMT-2 for 8 h under 1 MPa load, 1 m/s sliding velocity and 293 K ambient temperature. The counterbody material was steel 45 of 44 HRC and Rₐ = 0.3-0.4 μm. The run-in was performed at 100 kPa load till a complete contact over the whole friction surface. The friction coefficient and the wear rate were determined for a stationary friction mode without lubrication. The presented values of tribological characteristics are averaged over three measurements.

4. Results and discussion

There are two problems to be solved by mechanical activation of the powder composite components based on copper-CCNF. Firstly, the agglomerates formed of stuck together carbon nanostructures break under the applied energy effect; secondly, some mechanical bonding is gained between nanoparticles and microparticles of the composite components.

Copper powder particles are known to have a dendritic structure (Fig. 2). When a moving unit of the mechanical activator hits a metal particle with carbon nanostructures stuck to its surface, they undergo mechanical bonding. We can distinguish here two particular cases. In the first one, carbon nanostructures appear between the dendrites of the metal powder particles, and after the impact the nanostructures stick to the powder particles in the spaces between the dendrites. In the second case, the nanostructures imbed directly onto the dendrite surface. The results of microstructural investigations illustrated in Fig. 3 and Fig. 4 have proved this supposition.
periodic system. The number of secondary electrons depends on the atomic number of the element too, although to a lesser and less predictable degree. In a general case, the secondary electron emission factor changes but slightly with the atomic number so that the contrast is not commonly observed in this mode [22, 23]. It is seen from the figure that there are no carbon nanostructures on the copper particle surface, which also speaks in favor of the fact that the whole CCNF is found in the spaces between the particles of the powder composite. The described structure of the composite material is undesirable since it raises the probability of material softening. Notice that certain amount of contaminants is observed on the copper particle surface, being also an obstacle for the sintering process.

Figure 3. Copper particle surface in a non-activated powder system copper-carbon nanostructures: a – in reflected electrons; b – in secondary electrons.

Figure 4 presents images of structural fragments of the powder composite material copper-CCNF produced by electrocontact sintering and having the components subjected to preliminary mechanical activation. It is evident that the mechanical activation of dispersed components enables to fix some amount of carbon nanostructures on the surface of the metallic matrix of the powder composite material.

Figure 4. Copper particle surface in activated powder system copper-carbon nanostructures: a, c – in secondary electrons; b, d – in reflected electrons.

Duration of process of activation is of great importance for uniform distribution carbon nanostructures in a composite material. The longer the time of mechanical activation the more intensive is saturation of the surface layer of copper particles by carbon nanostructures and the better are the resultant physico-mechanical properties of the material. The investigation results have proved that the optimal time of treatment is about 60 min (see Table 1). The longer mechanical treatment reduces strength of the powder composite material while its porosity increases, which is, probably, connected with the beginning of agglomeration of the metal matrix particles and disturbance of homogeneity of the system.

Table 1. Effect of mechanical activation time on properties of obtained materials.

<table>
<thead>
<tr>
<th>Mechanical activation time (min)</th>
<th>Porosity (%)</th>
<th>Hardness (HB)</th>
<th>Compressive strength limit (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6...7</td>
<td>90...95</td>
<td>226...230</td>
</tr>
<tr>
<td>40</td>
<td>4...5</td>
<td>100...105</td>
<td>244...248</td>
</tr>
<tr>
<td>60</td>
<td>3...4</td>
<td>110...115</td>
<td>260...264</td>
</tr>
<tr>
<td>80</td>
<td>5...6</td>
<td>95...100</td>
<td>220...223</td>
</tr>
<tr>
<td>100</td>
<td>6...7</td>
<td>90...95</td>
<td>215...220</td>
</tr>
</tbody>
</table>

The results of triboeengineering tests of sintered antifriction materials based on the copper matrix and CCNF are presented in Table 2. It is evident that with increasing CCNF content from 0.01 till 0.1 mass% the friction coefficient decreases monotonously.

Table 2. Friction coefficient and wear rate of powder composite material copper-carbon nanostructures.

<table>
<thead>
<tr>
<th>Concentration of combined carbon nanostructured filler in composite material (mass%)</th>
<th>Friction coefficient</th>
<th>Wear rate (μm/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.42</td>
<td>0.48</td>
</tr>
<tr>
<td>0.02</td>
<td>0.35</td>
<td>0.29</td>
</tr>
<tr>
<td>0.03</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>0.04</td>
<td>0.28</td>
<td>0.16</td>
</tr>
<tr>
<td>0.05</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>0.06</td>
<td>0.2</td>
<td>0.09</td>
</tr>
<tr>
<td>0.07</td>
<td>0.17</td>
<td>0.06</td>
</tr>
<tr>
<td>0.08</td>
<td>0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>0.09</td>
<td>0.105</td>
<td>0.26</td>
</tr>
<tr>
<td>0.1</td>
<td>0.095</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Simultaneously, the wear rate dependence on CCNF content bears an extreme character. The minimal wear rate is shown by the composite material with CCNF content about 0.07 mass%. With further increment of the carbon filler concentration this parameter starts to grow and at CCNF concentration 0.1 mass% it reaches the level of the wear rate of the material containing only 0.01 mass% of CCNF.

The analysis of the friction coefficient values of the earlier developed powder copper-graphite antifrictional materials (Table 3) has visualized that this parameter approaches 0.2 when graphite concentration in the material reaches 25 mass%.

Table 3. Friction coefficient and wear rate of powder composite material copper-graphite.

<table>
<thead>
<tr>
<th>Graphite content in composite material (mass%)</th>
<th>Friction coefficient</th>
<th>Wear rate (μm/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.52</td>
<td>0.49</td>
</tr>
<tr>
<td>5</td>
<td>0.42</td>
<td>0.29</td>
</tr>
<tr>
<td>8</td>
<td>0.33</td>
<td>0.18</td>
</tr>
<tr>
<td>10</td>
<td>0.29</td>
<td>0.12</td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>25</td>
<td>0.20</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Notice, that this value of the friction coefficient is reached in the copper-CCNF composite already at 0.06 mass% concentration of CCNF, and it is below 0.1 at 0.1 mass% content. It is evident that
the minimum attained wear rate of the copper-graphite composite is 0.12 μm/km, which is by far higher in contrast to the minimum attained wear rate of the composite material copper-CCNF.

Microstructural investigations of the developed material have made grounds for a supposition concerning the impairment of tribotechnical characteristics. Figure 5a shows an AFM 3D image of a periodically repeating fragment of the composite material structure based on the powder system copper-CCNF. This fragment consists of five copper particles found in contact interaction. The investigations of the phase contrast of the fragment under study (Fig. 5b) has confirmed that carbon nanostructures are located mainly in the spaces between the particles of the metal matrix, although some negligible portion of CCNF is seen on the surface of copper particles (Fig. 6).

Figure 5. A fragment of composite material: a – 3D image; b – phase contrast.

Introduction of 0.06-0.07 mass% of CCNF makes it possible to a maximum and more uniformly fill the free interparticle spaces in the powder matrix avoiding softening of the sintering zones of copper powder particles. This increases density and improves antifrictional properties of the final material, decreasing thereby the amount of particles carried out from the friction zone. This also results in a corresponding elevation of the wear resistance of the antifrictional powder material, which adds service life to the material at operation in friction joints.

It should be noted that concentration of CCNF above 0.06 mass% in the composite based on the metallic matrix is insufficient to realize efficiently their unique antifrictional and strength properties. This results in impaired wear resistance of the composite and corresponding shortened life in friction joints. Worsening of service characteristics of the antifrictional powder composite material when concentration of carbon nanostructures makes up above 0.07 mass% takes place, most probably, because nanostructures that occur in the region of contact interaction between the components induce softening of the composite via screening copper-copper metal contacts. As a result, wear of the material augments and its lifetime in friction units reduces.

Figure 6. Phase contrast of a copper particle surface and CNT (shown by arrow) on its surface.

5. Conclusions

The effect of preliminary mechanical activation of components of the powder copper-CCNF system on the processes of distribution and embedding of nanostructural filler into the metal matrix has been studied experimentally.

The investigations have proved that preliminary activation of the powder system has promoted redistribution of carbon nanostructures over the metal matrix volume. It should be underlined that a certain portion of carbon nanostructures is transferred onto the surface and into the space between dendritic metal particles. As a result, the preliminary mechanical activation of the powder system has made grounds for obtaining more uniform distribution of carbon nanostructures in the metal matrix and mechanical bonding of some quantity of these structures on the surface of metal particles.

It has been also shown as a result of studies that time of mechanical activation of the initial components influences strength of the final composite material, and the time exceeding the optimal duration of mechanical activation may lead to strength impairment of the composite based on the copper-carbon nanostructure system.

The results of tribotechnical tests of the composite materials have proved that the optimal content of CCNF impregnated into the copper powder matrix is about 0.06-0.07 mass%. The composites with named concentration of nanostructural filler display the minimal wear rate along with a low friction coefficient. Microstructural investigations have visualized distribution of nanodispersed filler particles in the copper matrix. The preliminary mechanical activation of thus sintered powder system was proved to be efficient as it yields even enough distribution of CCNF in the metal matrix.

The described series of investigations has made provision for development of a powder composite material on the base of the copper matrix-CCNF system that is distinguished by high tribological properties. A combination of high tribotechnical and physico-mechanical characteristics open vistas for such composites for application in friction units of industrial equipment (bushing, plain bearing liner), electric and power engineering (movable contacts of electric machines).

The developed wear-resistant composite materials used in self-lubricating friction joints were subjected to experimental-industrial tests. The tests of the developed composite materials have proved them to be highly durable.
6. References


Acknowledgements

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