

Thermoexfoliated graphite — transitional metal nanocomposites

*T.A.Len, L.Yu.Matzui, N.G.Babich,
V.S.Kopan, L.M.Kapitanchuk**

T.Shevchenko National Kyiv University, Physics Department,
2 Acad. Glushkov Ave., 03680 Kyiv, Ukraine

*E.Paton Institute for Electric Welding, National Academy of Sciences of
Ukraine, 3 Bozhenko St., 01006 Kyiv, Ukraine

Composite materials (CM) have been obtained by chemical deposition of metal on graphite surface. It has been shown that TEG-nanoscaled transition metal CM can be prepared both by long-term salt decomposition on TEG surface and simultaneous reduction in hydrogen flow and by preliminary salt decomposition to metal oxide by thermal shock at high temperature. The application of "thermal shock" regime at the salt decomposition stage and metal oxide formation has been shown to result in metal particle formation possessing the size ten fold smaller than that in a case of "direct reduction". The metal particle size distribution obeys Gauss law and practically does not depend on metal component content.

Путем химического осаждения металла на поверхность графита получены композитные материалы (КМ). Показано, что КМ, содержащие терморасширенный графит (ТРГ) и наночастицы переходного металла, можно получить как путем длительного разложения соли на поверхности ТРГ с одновременным восстановлением в токе водорода, так и путем предварительного разложения соли до оксида металла в режиме высокотемпературного термоудара. Показано, что применение режима термоудара на стадии разложения соли и образования оксида металла позволяет получить частицы металла на порядок меньшего размера, чем в случае "прямого восстановления". При этом распределение частиц металла по размеру соответствует закону Гаусса и практически не зависит от содержания металлического компонента.

Nanostructured materials are an important group of physicochemical systems where it is possible to observe a lot of phenomena interesting by nature and important from practical point of view. The nanostructured state is able to provide a fundamentally new level of properties both constructional and functional materials. In order to obtain stable reproducible composites with a set of predetermined physicochemical characteristics, the main attention is given to study of functional correlations between chemical composition, technology, and structure of the obtained material [1]. Graphite-transition metal composite material (CM) is one kind of nanocomposite materials. Different types of carbon materials, such as nanotubes, fullerenes, activated coal,

disperse natural graphite as well as thermoexfoliated graphite (TEG) can be used as graphite matrix. The creation of CM on the base of thermoexfoliated graphite has been shown to be of good prospects [2]. There are different methods of metal fixing on the surface of graphite materials. According to the data presented in [3], application of the chemical deposition of metals on graphite matrix permits to obtain composite materials containing nanoscale metal particles on the surface of graphite support. The influence of the CM preparation method and the graphite support type on the distribution character of metal component and CM phase composition has been studied in [4, 5]. Experimental data on the influence of the metal salt type on the regularities of metal

particles formation (50 to 70 nm size) on the graphite support surface have been presented in [3]. Obviously, the application of different salt types and temperature-time regimes at the heat treatment of the salt-impregnated graphite material must also affect the distribution character of metal particles on TEG surface.

The main goal of this research was to investigate the influence of the temperature-time regimes of salt thermolysis and metal reduction on the graphite surface on topological and structure-phase characteristics of CM.

Thermoexfoliated graphite (TEG), i.e. graphite intercalated and heated to high temperature in a thermal shock regime [6], was used as carbon support to obtain CMs. The thermoexfoliated graphite is a porous material and possesses a high specific surface area. This satisfies the metal particles fixing conditions. Namely, the porous structure favors essentially the process of graphite support impregnation by metal salt solution. Besides, there are oxygen-containing groups at TEG surface, which proceed as active centers in nucleation and metal particles formation [3].

Nanocomposite materials have been prepared by chemical deposition of metal salts from aqueous solutions followed by thermal decomposition of salt under formation of the metal or metal oxide using the procedure described in [4]. This method is multi-stage process including graphite impregnation by salt solution; drying; thermal decomposition of salt with metal oxide formation on the surface of graphite support; and oxide reduction to pure metal. Thermodynamic and chemical conditions of each stage realization could obviously influence the morphology and topology of the obtained CMs.

TEG-Ni and TEG-Co samples with different metal content have been obtained. Ni and Co acetates have been used to prepare these CMs. The following different temperature-time regimes have been applied at the heat treatment stage of of the salt-impregnated graphite material: (i) the "direct reduction" regime including the metal salt decomposition and concurrent reduction of the salt-impregnated graphite material in a hydrogen flow at 350°C for 5 h; and (ii) the "thermal shock" regime including a rapid salt decomposition in the salt-impregnated graphite at 800°C during 12 s. This treatment results in formation of highly dispersed metal oxides. The further reduction

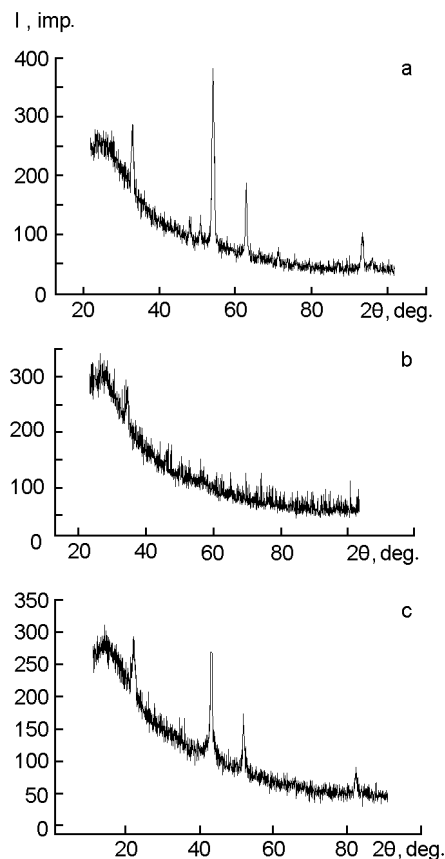


Fig. 1. X-ray diffraction patterns for composite materials: a — TEG-Ni (30 mass % Ni); b — TEG-Co (4 mass % Co); c — TEG-Co (25 mass % Co).

of metal oxide to the metal was performed in a hydrogen flow at 350°C for 5 h. The X-ray diffractometry (XRD) and electron microscopy (EM) were used to determine the phase composition and topology of the synthesized CMs. These investigations were performed using DRON-4-07 X-ray diffractometer (filtered Co K_{α} radiation), JSM-840 (Japan) and EMB-100AK electron microscopes.

Let the "direct reduction" regime be considered. The TEG-Ni CM (30 mass % Ni) was obtained by $NiAc_2$ decomposition and concurrent reduction in hydrogen flow at $T = 350^{\circ}C$ for 5 h. Fig. 1a displays the XRD pattern obtained for TEG-Ni CM. Graphite and Ni reflections are present in this pattern. Ni reflections are intense enough. The metal particle size has been determined from the analysis of the coherent scattering regions (CSR). That size is $L \approx 50$ nm (Table).

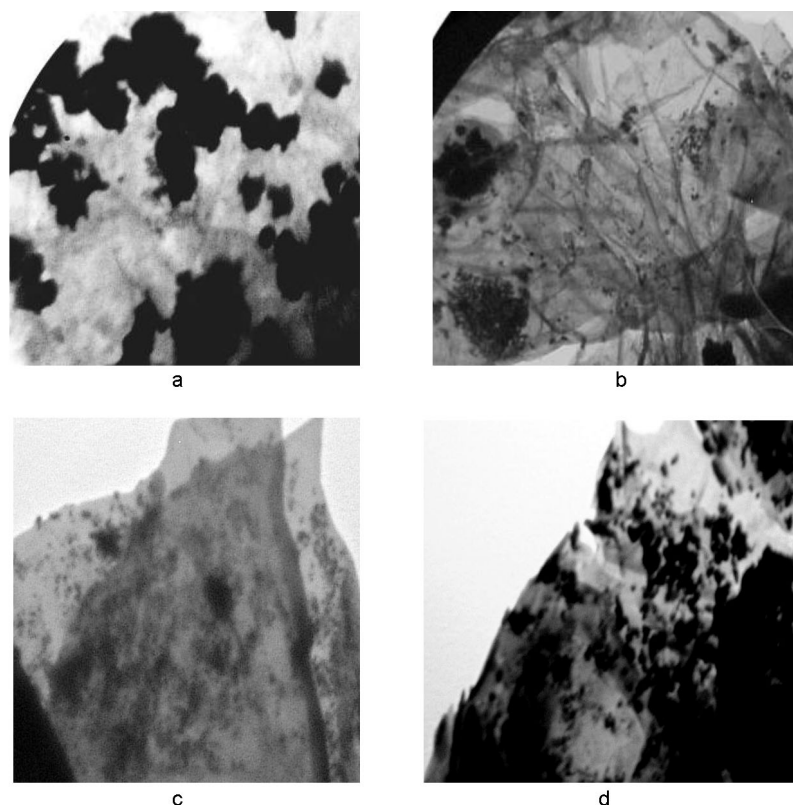


Fig. 2. TEM images of CM: a), b) TEG-Ni; c) TEG-Co (4 mass % Co); d) TEG-Co (25 mass % Co).

The EM investigations of the synthesized CMs were performed to study the topology and particle size distribution. Fig. 2a,b presents TEM images of TEG-Ni CM. As it is seen from these Figures, the metal particles are formed both on TEG surface and in pores. The particles of different shape are present. Large particles (250 nm size) are of triangular, rhombic, and hexagonal shape. This evidences the particles of such size possess crystal structure. The small particles are shapeless. The particles size distribution has been determined using the electron microscopy data (Fig. 3). As it is seen from Figs. 2a,b and 3, Ni particle size varies within wide limits. The particles of 10 to 90 nm size form the dominant part at the presented image. Besides, Ni particles from 120 to 430 nm size are also present.

Fig. 4a presents the data of TEG-Ni CM studies using scanning electron microscopy (SEM). The analysis of the obtained images evidences the presence both of small particles and particles accumulations (conglomerates) of 55 to 950 nm size. These conglomerates are shapeless, possess a loose structure and inhomogeneous size. As it is seen from Fig. 4a, the metal particles are uniformly distributed over the whole graphite surface. Thus, the application of the direct reduction at $T = 350^{\circ}\text{C}$ for 5 h results in formation on graphite surface of crystalline metal particles.

The investigations of TEG-Co CMs were performed in order to reveal the influence of both the preliminary thermal shock and the salt concentration on the metal particle distribution character on TEG surface. Figs.

Table. The mean sizes of metal particles in TEG-transition metal CMs determined by different methods

Samples	Regime	L , nm (CSR)	L , nm TEM	L , nm (SEM)
TEG-Ni (30 mass %)	Direct reduction	62	(10–340)	(53–950)
TEG-Co (25 mass %)	High-temperature thermal shock	46	(2.5–75)	(53–650)
TEG-Co (4 mass%)	High-temperature thermal shock		(6–70)	(59–180)

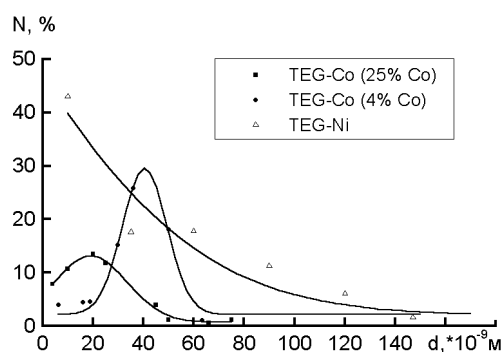


Fig. 3. Particle size distribution determined using the electron microscopy data.

1b,c display XRD patterns for TEG-Co CMs containing 4 and 25 mass % Co. Consideration of the obtained X-ray data evidences that the metal particles in these CMs are in fine-crystalline and quasi-amorphous state. Only graphite reflections are present in the XRD pattern for TEG-Co CM containing 4 % Co. The reflections corresponding to graphite and *fcc* Co are present at the diffraction pattern for TEG-Co CM containing 25 % Co. Co reflections are characterized by a broad pedestal. This evidences a large amount of nanoscale metal particles in this material. From the analysis of CSR, the mean size of Co particles has been determined to be not larger than 46 nm.

Fig. 2c presents a TEM image of TEG-Co CM containing 4 mass % Co. Co particles of 6 to 70 nm in size are observed over the whole sample area. The particles are shapeless and uniformly distributed in the bulk material. There are, however, metal particle aggregates near the fractures of graphite planes. Fig. 2d displays TEM image of a TEG-Co sample containing 25 % Co. Co particles agglomerations are observed on graphite surface. The size of Co particles ranges from 5 to 75 nm. From the data of X-ray studies, it can be concluded that metal formations consist of one or two crystallites. The formations of >100 nm size are conglomerates consisting of such "fine-crystalline" particles, but these particles are not accreted. The particles are also shapeless (as in a case of TEG-Co CM containing 4 % Co).

The size distribution of Co particles (see Fig. 3b) has been determined from electron microscopy data. The size distribution curve (for TEG-Co CM containing 4 % Co) exhibits a narrow maximum near 40 nm. 76 % of the total amount of particles are of (40±10) nm size. As to the TEG-Co CM with Co content 25 % (mass), the Co size distri-

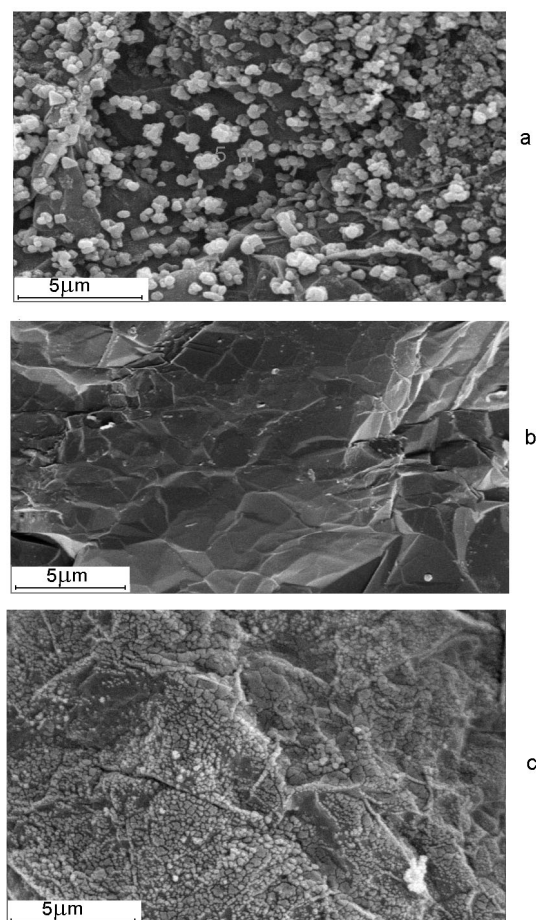


Fig. 4. SEM images of CM:

- a) TEG-Ni; b) TEG-Co (4 mass % Co);
c) TEG-Co (25 mass % Co).

bution curve exhibits a broad maximum near 20 nm (see Fig. 3b). 56 % of Co particles possess mean size of (20±15) nm. Thus, if the high-temperature thermal shock is used at the stage of metal oxide formation (just this regime has been used to prepare TEG-Co specimens), the size distribution curve exhibits a maximum, being independent on metal content. Such distribution could be approximated by the Gauss function. However, the maximum is sharp at low metal content, while at higher metal content, it is broadened and shifted to the larger metal particle sizes. Such values of Co particle sizes in TEG-Co CM agree with the data obtained by scanning electron microscopy (Fig. 4b). According to these data, metal particle size varies from 55 to 650 nm. So, metal particles in TEG-Co CM are smaller than in TEG-Ni CM. The mean sizes of metal particles in TEG-transition metal CMs determined by different methods are listed in Table. Thus, application of

thermal shock at the stage of salt decomposition and metal oxide formation leads to the comminution of metal particles in CM.

To conclude, the possibility to obtain TEG-nanoscaled transition metal CM both by long-term salt decomposition on TEG surface and simultaneous reduction in a hydrogen flow and by preliminary salt decomposition to metal oxide by high-temperature thermal shock has been shown. The "direct reduction" regime has been shown to provide the formation of metal particles of 10 to 340 nm in size. In this case, 70 % of the particles are of 10 to 90 nm size. 30 % of the particles possess the sizes varying from 90 to 340 nm. The application of "thermal shock" regime at the stage of salt decomposition and metal oxide formation has been shown to result in metal particle formation possessing the size by one decimal order smaller than that in the case of "direct re-

duction". Here, metal particle size distribution obeys Gauss law and practically does not depend on the metal component content.

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Нанокompозити — терморозширений графіт-перехідний метал

*Т.А.Лень, Л.Ю.Мацуї, М.Г.Бабич,
В.С.Копань, Л.М.Капітанчук*

Шляхом хімічного осадження металу на поверхню графіту одержано композитні матеріали (КМ). Показано, що КМ, які містять терморозширений графіт (ТРГ) та наночастинки перехідного металу, можна одержати як шляхом тривалого розкладу солі на поверхні ТРГ з одночасним відновленням у потоці водню, так і шляхом попереднього розкладу солі до оксиду металу в режимі високотемпературного термоудару. Показано, що застосування режиму термоудару на стадії розкладу солі та утворення оксиду металу дозволяє одержати частинки металу на порядок меншого розміру, ніж у випадку "прямого відновлення". При цьому розподіл частинок металу за розміром відповідає закону Гаусса і практично не залежить від вмісту металевого компоненту.