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Influence of heat treatment on morphology and phase composition of TEG-Co composite material

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The influence of ageing and heat treatment on the structure, phase composition and morphology of cobalt supported composite material TEG + 30 mass.% Co prepared by chemical deposition method has been studied using the X-ray diffraction, scanning electron microscopy, the Auger spectroscopy and SIMS. Heat treatment of the studied materials results in phase transformations within the metal component consisting in the formation of complex cobalt oxide and cobalt carbide phases. After heat treatment the shape of modifier particles remains similar to that in as-prepared composite material whereas their size drastically increases that may evidence the recrystallization processes accompanied by the metal-modifier particle segregation.

Методами рентгеновского фазового анализа, сканирующей электронной микроскопии, Оже-спектроскопии и ВИМС исследовано влияние старения и термической обработки на структуру, фазовый состав и морфологию фаз в композиционном материале ТРГ + 30 масс.% Co, полученном методом химического осаждения. Термобработка исследуемого материала вызывает фазовые превращения в металлической компоненте композита, заключающиеся в формировании сложных карбидных и оксидных фаз на основе кобальта. В результате термической обработки форма частиц модификатора остается подобной таковой для свежеизготовленного композита, а их размер существенно возрастает, что может свидетельствовать о процессах рекристаллизации, сопровождающихся сегрегацией частиц металла-модификатора.

Recently, nanostructured magnetic materials have attracted an increasing interest due to possibilities of their application in integrated and magnetoelectronic devices such as sensors, spin valves, high-density magnetic recording media, etc. [1, 2]. Co-based amorphous metallic systems (e.g. Co–Zr, Co–Ti) [3] are known to have high saturation magnetization and unique soft magnetic properties. The levels of soft magnetic properties comparable to those of Co-rich amorphous alloys were also achieved in nanocrystallized Co-rich alloys [4]. On the other hand, an important feature of some systems, such as "carbon-nanostructured Co", which were intensively studied recently [1, 5], is the increasing of the effective distance between neighboring magnetic particles. So, the exchange coupling between them is essentially weakened, that, in turn, could result in reducing of media noise. Besides, formation of the carbon-encapsulated structures provides a protection against surface oxidation of metallic grains that is a factor of importance from the application stand point. The importance is due to the fact that even minor amounts of oxides could make a dramatic influence on magnetic performance properties of nanostructured composite materials (CM) [6]. Such materials were already prepared using various methods, including the carbon arc technique, the tungsten arc technique, ion-beam and magnetron Co-sputtering, the *rf*-plasma technique, etc.

[2, 4, 7]. The natural mutual solubility of C and Co is extremely low and metastable cobalt carbides are decomposed even at low temperature annealing. So, Co–C system is a good candidate to produce composite materials. Before [8], we have reported a method of Co–C composite materials preparation by chemical deposition of Co on the surface of thermoexfoliated graphite (TEG) from aqueous salt solutions. The structure of Co particles in this material was shown to be essentially nonequilibrium: the X-ray phase analysis proved the presence of both *f.c.c.* and amorphous cobalt in the as-prepared material. That is why one can expect variation of the structure and, correspondingly, the properties of such CMs under various external actions, i.e an important problem of their stability arises.

Thus, the main purpose of this work is to study the stability of cobalt supported CM on the base of TEG and the influence of heat treatment under various conditions on their morphology and phase composition, the CM containing 30 mass.% Co being selected as representative sample.

The composite material of Co–C system containing 30 mass.% Co was prepared by chemical deposition of cobalt on TEG surface. Graphite was preliminary thermoexfoliated using the procedure described in [9]. Cobalt acetate $Co(CH_3COO)_{20}\cdot 4H2O$ was used as the cobalt source. The TEG samples of 1.5 g mass were impregnated by into an appropriate amount of cobalt acetate aqueous solution, kept for 10–12 h under continuous mixing and dried at 150°C. Then the samples were exposed to thermal shock at 800°C for 12 s. The obtained material was reduced at 300–350°C in a hydrogen flow. As a result, cobalt modifier particles were deposited on the surface of TEG due to several successive chemical reactions [9, 10]. The subsequent heat treatment of the synthesized material was performed in a resistance furnace under controlled gas atmospheres.

The phase composition of the treated composites was determined by X-ray phase analysis (DRON-4 diffractometer, filtered CoK_α-radiation). Scanning electron microscopy (JSM-840 microscope) was used to study morphology, shape, and distribution of Co particles on the TEG surface. LAS-2000 system ("Riber", France) was used to determine the elemental composition of the obtained materials by their Auger spectra (the energy of primary electronic beam was 3 keV, the probe current 0.5 µA). It becomes possible to detect the element distribution in the sample depth by the surface ion etching (the etching rate was usually 3 nm/min). SIMS technique being also realized in the LAS-2000 system was used to refine the elemental composition of subsurface layers and to determine the possible types of the chemical compounds being formed. The etching rate in this case was 0.3 nm/min. Magnetic susceptibility at room temperature, χ_{300}, was determined using the Faraday technique with automatic microbalance (the accuracy was within 1.5 %).

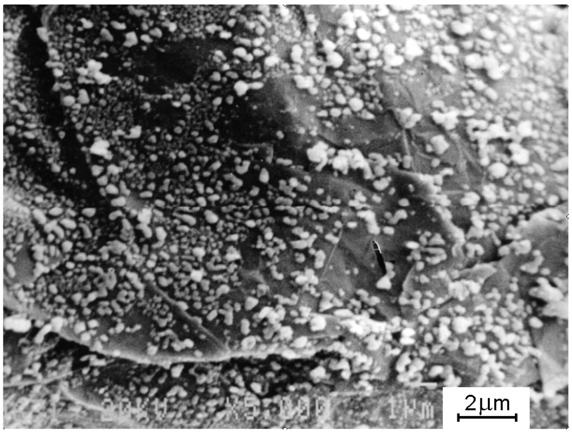

Fig. 1. SEM image of the surface of as-prepared TEG + 30 % Co composite material.

In what follows, presented is the detailed investigation of the morphology and phase composition of TEG + Co (30 mass. % Co) composite materials obtained by chemical deposition method focusing at the influence of heat treatment under controlled gas atmospheres.

Fig. 1 is the SEM image of Co particles deposited on TEG surface. The as-prepared composite material is seen to consists of dispersed globular Co particles distributed nearly uniformity on the developed graphite surface. Along with relatively large-scale (200–400 nm in size) Co particles, relatively small (~50 nm) ones are formed on TEG surface. It is seen that the large metal particles are conglomerates formed due to coagulation of smaller particles of several dozen nanometers in size. This is also confirmed by the X-ray diffraction analysis data for such materials reported in [8] which indicate that Co particles in the investigated CM consist of highly disordered (or even amorphous) Co-based phase and crystalline finely dispersed *f.c.c.* Co phase. In addition to our earlier studies, the ele-

Table 1. Elemental composition of as-prepared TEG + 30 mass.% Co (at.%)

Etching time, min	C	O	Co	S	Cl
0.0	97.1	1.6	1.0	0.1	0.2
0.2	95.5	2.0	2.2	0.1	0.2
0.6	93.3	1.6	5.0	0.1	0.1
1.0	94.5	0.4	5.0	0	0.1
2.0	94.0	0.2	5.8	0	0
4.0	93.7	0	6.3	0	0
7.0	93.7	0	6.3	0	0
10.0	93.5	0	6.5	0	0
15.0	93.6	0	6.4	0	0
20.0	93.5	0	6.5	0	0
25.0	93.8	0	6.2	0	0
30.0	94.0	0	6.0	0	0
40.0	95.2	0	4.8	0	0
max.	7.9	3.2	88.9	0	0

ment content of TEG + 30 mass.% Co CM subsurface layer was analyzed by the Auger spectroscopy method. The data are summarized in Table 1 (etching rate 3 nm/min). The Table 1 data for different etching times are averaged over the scanning area of 1×1 mm^2. However, sites considerably enriched in Co are observed (*max* line in Table 1). Such sites correspond obviously to locations of modifier particles on TEG surface. Just these sites were subjected to the Auger spectroscopy investigation in the heat-treated samples. The data obtained show the presence of oxygen and small amounts of sulfur and chlorine (the technological impurities) together with basic elements (Co, C). The S and Cl impurities were detected only in a very thin layer (several nanometers), oxygen was detected in the 15–30 nm thick surface layers. It is most likely that oxygen is incorporated into cobalt oxide, which is formed on metal particle surface because the maximal oxygen concentration was observed for the same sites of the sample surface where the maximal cobalt content has been detected. Some amount of carbon was also found for these parts of the sample surface. Thus, one can conclude that Co particles are covered by thin layer of oxide (most likely, Co_3O_4 [7]) and containing Co and C are deposited on TEG surface.

Such structure of Co particles, i.e., the presence of Co-based phase with nonequilibrium (distorted) structure, has been also confirmed by the magnetometric investigations presented in [8], which displayed thermomagnetic behavior of the synthesized CM that is similar to that for ferromagnetic amorphous alloy [11]. Taking into account the finding reported in [8] and the data of the Auger analysis of as-prepared CM (Table 1), one can conclude that carbon is acting, evidently, as a glass-forming impurity that stabilizes the nonequilibrium structure of the subsurface layers of Co particles.

It is known that such phase is not in equilibrium thermodynamically and relaxes to more equilibrium state. Moreover, the relaxation process could take place even at low temperatures [11]. Just due to this process, the maximum on $\chi(T)$ curves was not observed for CM aged at room temperature for 5 months [8], although the structure of material remains still nonequilibrium. So, various external actions such as, for example, thermal or thermomagnetic treatments should be expected to result in changes of CM morphology, phase composition and structure. To confirm this suggestion, we performed different treatments of the synthesized metal-carbon composite.

Table 2. Phase composition and magnetic susceptibility of the heat-treated TEG + 30 % Co

Sample	Kind of treatment	Phase composition	χ_{300}, 10^{-6} cm^3/g
as-prepared	—	*C* + *f.c.c.*Co + amorph. phase	9400
1	ageing at room temperature	C + *f.c.c.*Co + amorph.phase	8700
2	annealing at 850 K, 8 h, 1 Pa (air)	*C* + *f.c.c.* Co+CoO	2400
3	annealing at 850 K, 8 h, 10^{-2} Pa (air)	*C* + *f.c.c.*Co	8300
4	annealing at 770 K, 6 h, on air	C + Co_3O_4	~0
5	annealing at 850 K, 6 h, 10^4 Pa (Ar) (after treatment 4)	*C* + *f.c.c.*Co + CoO	570
6	annealing at 850 K, 6 h, 10^4 Pa (Ar)	*C* + *f.c.c.*Co	8200

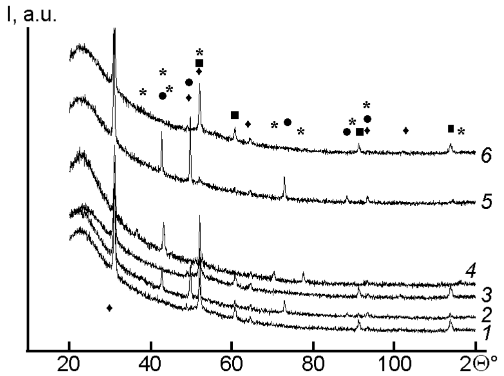

Fig. 2. X-ray diffraction patterns of TEG + 30 % Co composite (numbering of curves corresponds to that in the Table): ♦ — graphite, ■ — f.c.c. Co, • — CoO, * — Co_3O_4 (spinel-like structure).

First of all, the ageing of CM for 5 months results in some decrease of susceptibility at room temperature χ_{300} (see Table 2). Such effect could be considered as a result of interaction of composite material with the air components. The increase of H^+, CoO^-, $CoOH^-$ and Co_2H^- ion yield detected in SIMS experiments on aged samples confirms the above assumption. Phase composition after such ageing, according to the X-ray diffraction data, is not changed as compared to that for as-prepared CM [8]. But halo in the vicinity of (111) *f.c.c.* Co reflection becomes less pronounced. The appropriate diffraction pattern for the aged TEG + 30 % mass. Co is presented in Fig. 2 (curve 1).

To investigate the peculiarities of phase composition changes of the obtained composites and stability of their phases, the samples were subjected to heat treatment under different conditions: different kinds of atmosphere, residual pressure, time and temperature. The kinds of treatment are listed in Table 2. Fig. 3 presents SEM images of TEG + 30 % Co surface after such treatments. The particle shape was found to be similar for all cases and similar to that in as-prepared material (Fig. 1): the particles are of globular or globe-oblong shape, but their size is greater than in as-prepared sample. The mean size of the particles was estimated to be of 150 nm (treatment 2), 350 nm (treatment 3), about 400 nm (treatment 4) and 700 nm (treatment 5). As it is clearly seen in Fig. 3, the large-scale particles consist of joint small particles less than

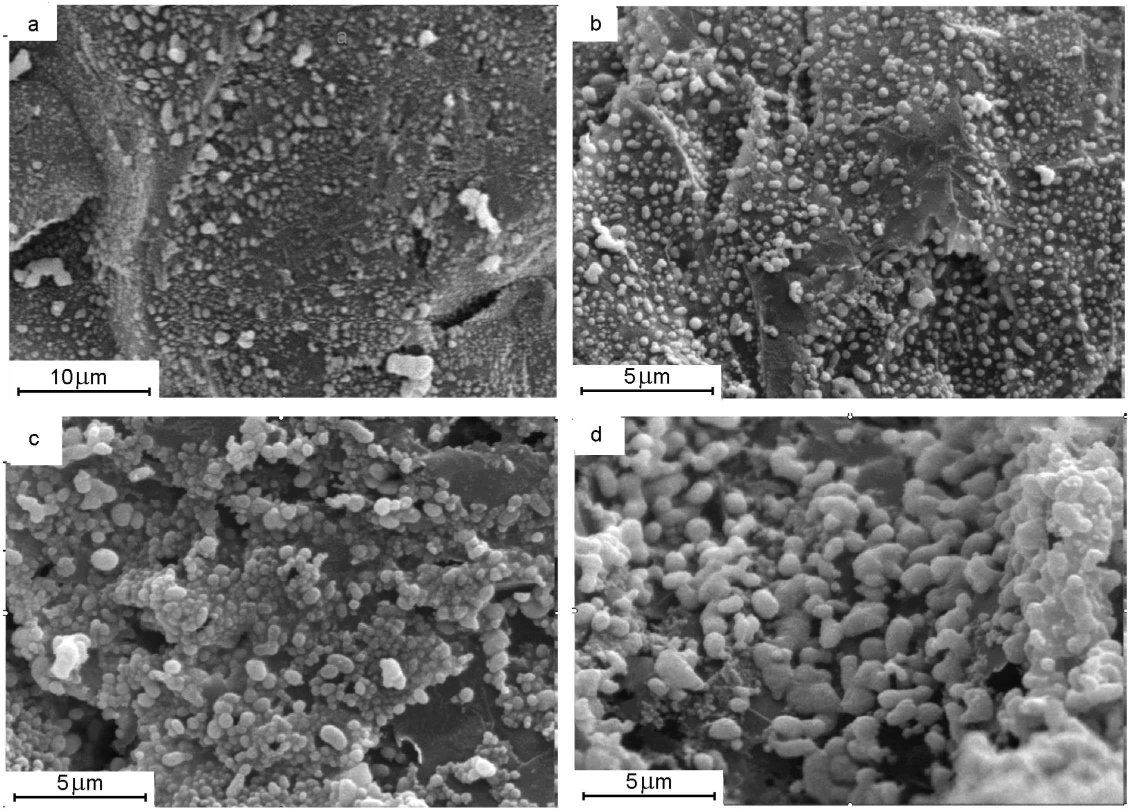

Fig. 3. SEM images of the TEG + 30 % Co composite surface treated at different regimes: a — 2, b — 3, c — 4, d — 5.

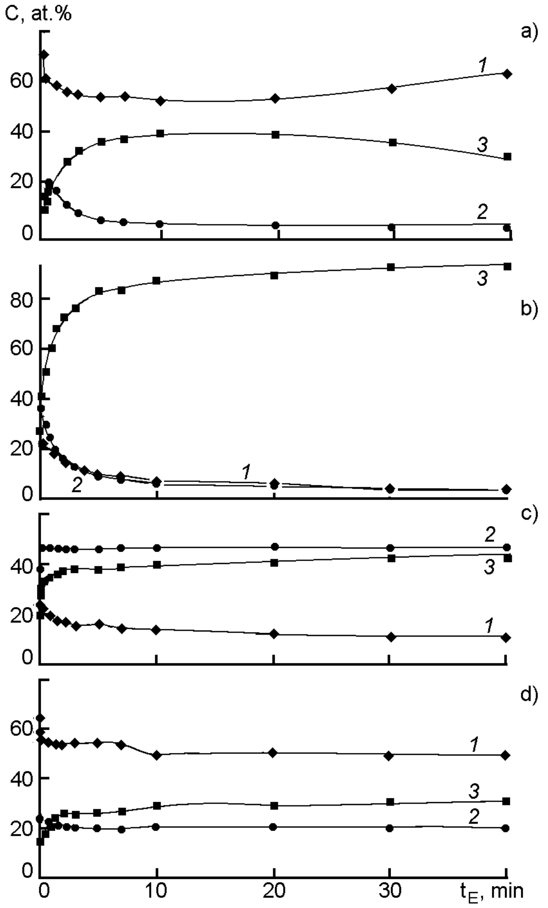

Fig 4. Components distribution in the depth of TEG +30% Co composite treated at different regimes: a — 2, b — 3, c — 4, d — 5.

100 nm in size. So, recrystallization processes accompanied by the metal-modifier particles segregation take place in sample under heat treatment. Phase composition of the sample after treatment 3 according to the X-ray diffraction data (Fig. 2, curve 3) corresponds to the mixture of graphite and *f.c.c.* Co phases, moreover, the width of diffraction reflections of the latter phase decreases as compared to the as-prepared and aged samples. Besides, a shift of *f.c.c.* Co diffraction peak is observed which could be associated with particle structure changes. The same phase composition was observed for the samples annealed at 850 K for 6 h in purified argon atmosphere (Fig. 2, curve 6). The formation of cobalt oxides (CoO and Co_3O_4) was found by the X-ray diffraction under treatments 2, 4, 5 (see Fig. 2).

The depth distribution of elements for the treated samples determined by the Auger spectroscopy is presented in Fig. 4 (the etching rate 3 nm/min). Evidently, the cobalt particles covered by thin (up to 5 nm) oxidized surface layer are distributed on the surface sample, annealed at 850 K in 10^{-2} Pa vacuum for 8 h. The oxygen content in the particle volume was found to be less than 3 at.%. The content of oxygen in the material annealed under residual pressure of 1 Pa at 850 K, 8 h is some higher (up to 4 at.%). The thickness of the oxidized surface layer is about 10 nm. This fact allows to determine the structure of this layer by the X-ray powder diffraction as CoO (Fig. 2, curve 2). The particles of metal-modifier on the surface of sample annealed in air at 770 K for 6 h are in a form of oxide or carboxide (hydrogen could not be detected by the Auger spectroscopy). Their stoichiometric composition was found to be close to Co_3O_4, that is confirmed by the X-ray diffraction studies (Fig. 2, curve 4). The subsequent annealing of these samples at 850 K for 6 h in argon atmosphere results in decomposition of Co_3O_4. In this material *f.c.c.* Co and CoO have been found by X-ray diffraction (Fig. 2, curve 5).

Additional data have been obtained by SIMS investigations. Those are summarized in Table 3 and prove the possibility of the formation of cobalt oxides, carboxides, carbides and hydroxides. In particular, SIMS spectra show that the release of the CoC^+, Co_2C^+ and $Co_2C_2^+$ ions is observed for the samples treated in atmosphere with low content of oxygen together with the outcome of the C^+, Co^+, Co_2^+ which are the main components of material. Moreover, their amounts exceed those for the as-prepared samples. This evidences the formation and strengthening of the Co–C interatomic bonds and, therefore, the creation of the Co_nC carbide phase in subsurface layers of metal particles. Probably, this carbide phase is Co_3C, since other known carbide Co_2C is decomposed even at 300 °C [12]. The formation of cobalt carbide is also reflected in the decreasing of magnetic susceptibility value χ (see Table 2) since a part of Co atoms are bound in nonmagnetic carbide phase. The data presented evidence also that the annealing in oxygen-containing atmosphere results in cobalt oxide phases formation (CoO or Co_3O_4 with spinel-like structure). Moreover, the type of formed oxide depends on oxygen partial pressure in gas atmosphere. The magnetic susceptibility values of the treated samples are essentially smaller than those for the as-prepared material. It is necessary to note that the structure inherent in the as-prepared CM remains stable up to the temperature of about 500 K [8], which defines

Table 3. The yield of single-charged ions for the heat-treated TEG + 30 % Co (the numbering of treatment corresponds to that in Table 2)

Mass	Ion	Kind of treatment			
		2	3	4	5
Positive ions					
1	H	359	328	200	294
2	H_2	5	3	6	8
16	O	21	3	50	76
59	Co	7490	2810	4678	7525
71	CoC	77	49	38	62
75	CoO	45	10	67	98
76	CoOH	25	9	14	35
83	CoC_2	23	35	6	16
87	CoCO	25	9	11	25
88	CoCOH	11	8	9	1
99	CoC_2O	9	27	24	18
103	$CoCO_2$	19	3	0	1
115	CoC_2O_2	41	45	34	67
118	Co_2	845	645	686	1343
119	Co_2H	23	35	6	38
130	Co_2C	47	33	17	48
134	Co_2O	41	17	60	106
142	Co_2C_2	31	24	11	25
Negative ions					
1	H	4460	3480	3062	6511
16	O	4690	939	8662	13877
17	OH	1170	247	1103	1966
18	H_2O	8	0	20	24

the service temperature range of this material.

In conclusion, TEG + 30 mass.% Co CM prepared by chemical modification method consists of dispersed globular Co particles with essentially nonequilibnum structure distributed nearly uniformly over the developed TEG surface. According to the Auger spectroscopy, Co particles in the synthesized composite material are covered with a thin oxide layer and contain a certain amount of carbon, which could act as glass-forming element. After heat treatment, the shape of modifier particles remains similar to that in as-prepared CM, whereas their size increases that may evidence the recrystallization processes accompanied by the metal-modifier particle segregation. The Auger spectroscopy, SIMS and X-ray investigations of CM subjected to different kinds of heat treatment show the formation of complex cobalt carbide and cobalt oxide phases.

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Вплив термообробки на морфологію та фазовий склад композитних матеріалів ТРГ-Co

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Методами рентгенівського фазового аналізу, скануючої електронної мікроскопії, Оже-спектроскопії та ВІМС досліджено вплив старіння і термічної обробки на структуру, фазовий склад і морфологію фаз у композиційному матеріалі ТРГ + 30мас.% Co, одержаному методом хімічного осадження. Термообробка досліджуваного матеріалу викликає фазові перетворення у металічній компоненті композиту, а саме — формування складних карбідних і оксидних фаз на основі кобальту. В результаті термічної обробки форма частинок модифікатора залишається подібною такій для свіжовиготовленого композиту, а їх розмір суттєво зростає, що може свідчити про процеси рекристалізації, які супроводжуються сегрегацією частинок металу-модифікатора.