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Thermomagnetic studies of thermoexfoliated graphite-transition metal composites

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Thermal stability and magnetic susceptibility of thermoexfoliated graphite-metal (TEG-Me) composites have been investigated in the temperature range 300–850 K. The TEG-Me (Co, Ni) composites have been produced by the metal cation reduction in aqueous medium with sodium tetrahydroborate. The structure and phase composition of the products was characterized using X-ray diffraction, scanning electron microscopy, Auger electron spectroscopy and secondary ion mass spectrometry. The results of these investigations show that the metal in the green composites must exist in the bound state as Me–B and Me–H. The gradual heating (up to 850 K) or annealing (at 825 K) of the TEG-Me composites results in the appearance of ferromagnetic properties. Thermal cycling of TEG-Me composites results in a decreased magnetic susceptibility due to oxidation of metallic particles.

Проведены исследования термической стабильности и магнитной восприимчивости композитов терморасширенный графит-металл (ТРГ-Ме) в температурном интервале 300–850 К. Композиты ТРГ-Ме(Co, Ni) приготовлены методом восстановления катионов металла в водном растворе тетрагидроборатом натрия. Структурно-фазовый состав композитов определялся при использовании методов рентгеновской дифракции, сканирующей электронной микроскопии, Оже- и вторичной ионной масс-спектрометрии. Полученные результаты этих исследований указывают, что металл в свежеприготовленных композитах находится, вероятно, в связанном состоянии в виде Ме–B и Ме–H. Постепенное нагревание (до 850 К) либо отжиг (при 825 К) композитов ТРГ-Ме приводит к возникновению ферромагнитных свойств. Термоциклирование образцов ТРГ-Ме приводит к уменьшению магнитной восприимчивости, что вызвано окислением металлических частиц.

Fixation of metal nanoparticles on different substrates is a very promising method in development of novel materials since it provides an unconventional combination of functional properties. The use of graphite materials as a support for production of graphite-transition metal composites is of good prospects due to the low density, resistance against aggressive environmental actions and easy production technology of those composites [1, 2]. The chemical deposition from aqueous salt solutions followed by thermolysis is used widely to produce supported metal nanoparticles. The fixation of magnetic transition metal (e.g., Fe, Co or Ni) particles on graphite surface [3] results in appearance of ferromagnetic properties in graphite-transition metal composites. The aim of this work was to investigate the phase composition, morphology, and thermal stability of thermoexfoliated graphite-transition metal (TEG-Me) materials and also the distribution of metal particles on graphite surface.

Graphite-metal composites were prepared by the metal cation reduction in aqueous solutions with sodium boron hydride ($NaBH_4$). This method is used widely to obtain the metals in nanodispersed state [4, 5]. We have used thermoexfoliated graphite (TEG) [6] and metal chlorides ($CoCl_2$ or $NiCl_2$) to obtain TEG-Co and TEG-Ni composites. The structure and phase composition of the synthesized TEG-Me composites were studied using the X-ray diffraction (DRON-4-07 X-ray diffractometer, filtered CoK_α emission), scanning electron microscopy (SEM) (JEOL JSM-840 instrument equipped with a Link Analytical X-ray microanalysis system), the Auger electron spectroscopy (AES) (LAS-2000 Riber spectrometer), and secondary ion mass spectrometry (SIMS). Temperature dependences of magnetic susceptibility $\chi(T)$ were studied using the Faraday technique within 300–850 K temperature range.

Fig. 1 shows SEM micrographs of TEG-Me composites. The surface of graphite particles is coated with spherical particles of about 0.2 μm size and flaky agglomerates (average size of about 2–10 μm). The metal component distribution in composites is inhomogeneous.

The XRD patterns of the as-prepared TEG-Co(Ni) powders show only trace reflections from pure metal (Co, Ni). Only graphite reflections have been observed, (Fig. 2). This could be conditioned either by low Me content in TEG or, alternatively, by small size of Me particles (less than 10 nm), or else the metal is present in bound state as Me–B and Me–H.

The presence of metal particles was confirmed by the results of the Auger-spectroscopy data for the composites (Fig. 3). Along with Co, an essential amount of B was found to be presented in these powders, that is confirmed also by the SIMS data.

The Co^+, B^+, H^- and O^- yields for the as-prepared TEG-Co composites were found to be much higher than those for Cl^- and Co^-. The signals of other ions were insignificant. These results indicate that the graphite-Co composites contain Co, B and much lower amounts of CoO and $CoCl_2$.

To evaluates the composite thermal stability, the graphite-Me powders were subjected to gradual heating up to 850 K and to annealing at 825 K for 1.5 h. Heating up to 850 K as well as annealing at 825 K have been found to cause phase transformations in the powders. Analysis of the XRD data indicates that heating of the TEG-Me

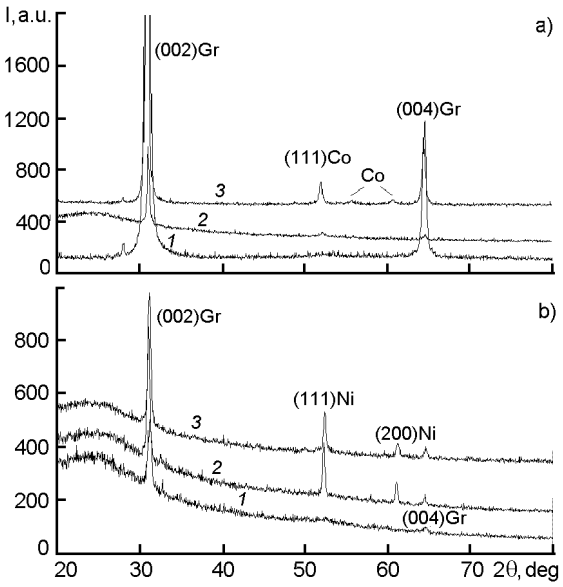

Fig. 1. XRD patterns of TEG-Me composites. (a) TEG-Co: (*1*) as-prepared (compacted), (*2*) after gradual heating to 850 K (powder), (*3*) annealed at 825 K for 1.5 h (compacted); (b) TEG-Ni: (*1*) as-prepared (compacted), (*2*) after gradual heating to 850 K (powder); (*3*) annealed at 825 K for 1.5 h (compacted).

composites to 825–850 K (Fig. 1, scans *2*, *3*) results in gradual formation of rather large metal particles, the diffraction peaks corresponding to the metallic phase arise in diffraction patterns for annealed TEG-Me samples. This seems to be related with the fact that TEG-Me composites include small amounts of Me–H and Me–B solid solutions that decompose under heat treatment into Me and H and Me and B, respectively. Besides, Me nanoparticles on the graphite surface in the TEG-Me powders agglomerate during heating and form larger particles.

An additional information concerning the phase transformations in the synthesized composites has been obtained from thermomagnetic measurements. The as-prepared TEG-Co composites exhibit weak magnetization slightly decreasing with temperature (Fig. 4a, curve *1*). Surprisingly, a sharp rise of magnetic susceptibility was observed for these samples starting from 640 K during gradual heating to 850 K. Such magnetic behavior could be caused by the presence of a substantial amount of boron and by the breaking of Co–B and Co–H bonds upon heating (as a result, Co-rich particles are formed possessing higher magnetization as compared to that of the as-prepared material particles). An alternative reason,

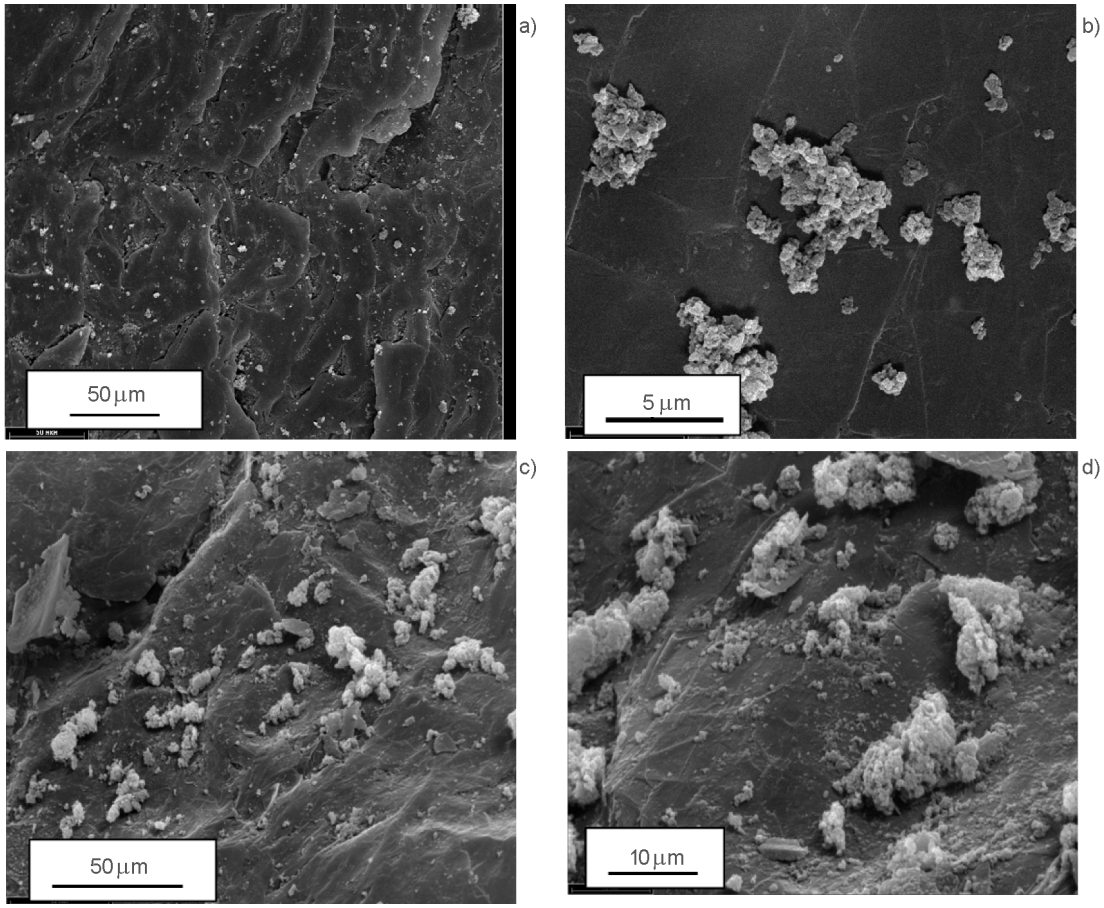

Fig. 2. SEM images of TEG particles, impregnated by metal chloride solution and reduced by sodium boron hydride solution into TEG-Me: — different parts of TEG-Co particle (a, b); — different parts of TEG-Ni particle (c, d); a, c — ×1000; b, d — ×4000.

namely, the agglomeration of fine Co particles, seems to be less significant, since the mean size of supported particles in the as-prepared material is about 100 nm.

In the case of TEG-Ni composite, the magnetization of the as-prepared material is much lower and almost independent of temperature (Fig. 5a, curve *1*). The heating of this composite up to 850 K results in appearance of ferromagnetism observed under cooling similar to pure nickel (curve *2*) with the Curie point about 630 K. The origin of such behavior is thought to be similar to that for TEG-Co composites. Thermomagnetic behavior of TEG-Me composites studied here differs from that of TEG-Co(Ni) CMs synthesized by metal salt thermolysis as reported in [7]. This transformation is also confirmed by the X-ray study results of heat-treated TEG-Ni samples (Fig. 1, diagram *2*): the reflections corresponding to metallic Ni phase have been observed. The annealing of as-prepared TEG-Me composites at 825 K for 1.5 h causes an increase

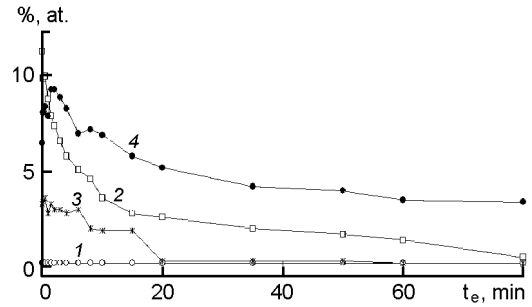

Fig. 3. AES depth profiles of the as-prepared TEG-Co composite, ion-etching rate of 5 Å/min: *1*, B; *2*, O; *3*, BO; *4*, Co.

of ferromagnetic properties in these composites (Figs. 4b and 5b). After first heating-cooling cycle of TEG-Me, we performed the repeated heating-cooling cycles and measured the magnetic susceptibility during these cycles. The gradual magnetic susceptibility decrease of TEG-Me samples was found during the thermocycling. In our opinion, the decrease of magnetic suscepti-

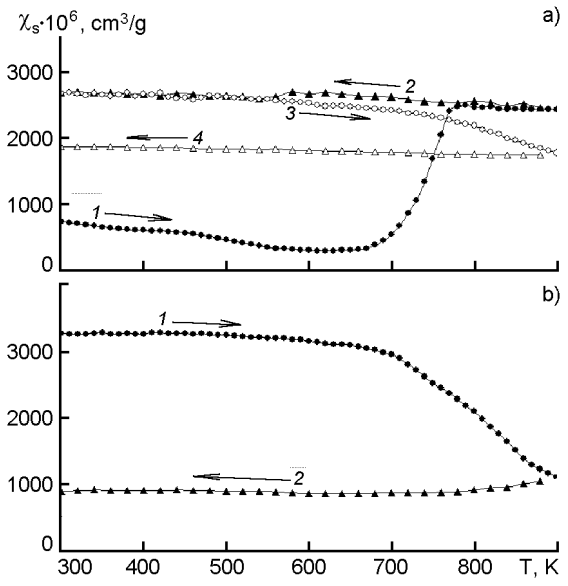

Fig. 4. Magnetic susceptibility as a function of temperature for graphite-Co composites: (a), as-prepared TEG-Co (*1, 2*) (1st heating-cooling cycle), (*3, 4*) — TEG-Co after heating up to 850 K (2nd cycle), respectively, (b), TEG-Co annealed at 825 K.

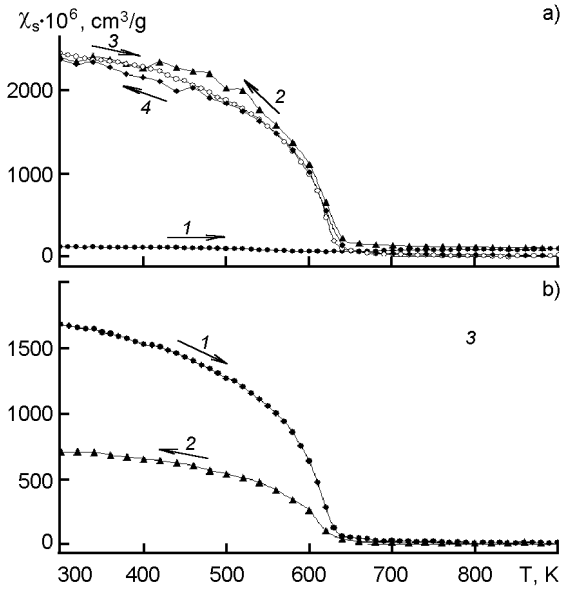

Fig. 5. Magnetic susceptibility as a function of temperature for graphite-Ni composites: (a), as-prepared TEG-Ni (*1, 2*) (1st heating-cooling cycle), (*3, 4*) — TEG-Ni after heating up to 850 K, (2nd cycle), respectively, (b), TEG-Ni annealed at 825 K.

bility in annealed TEG-Me composites after several heating-cooling cycles is due to partial oxidation of metal particles and decrease of ferromagnetic phase content.

References

1. E.B.Stails, Supports and Supported Catalysts: Theory and Practice, Khimiya, Moscow (1991) [in Russian].
2. G.Sirokman, A.Mastalir, *J. Catalysis*, **117**, 558 (1989).
3. A.Furstner A, F.Hofer, H.Weidmann, *Carbon*, **29**, 915 (1991).
4. N.N.Maltseva, Sodium Boron Hydride, Nauka, Moscow (1985) [in Russian].
5. M.V.Ivanov, K.M.Gorbunova, A.A.Nikiforova, B.P.Schedrin, *Dokl. Akad. Nauk SSSR*, **1999**, 1317 (1971).
6. E.I.Khar'kov, V.I.Lysov, L.Yu.Matzui et al., Ukrainian Pat. 33777A (2001).
7. M.Babich, L.Matzui, L.Vovchenko et al., *Mater. Sci. Forum*, **373–376**, 224 (2001).

Термомагнітні дослідження композитів терморозширений графіт-перехідний метал

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Проведено дослідження термічної стабільності та магнітної сприйнятливості композитів терморозширений графіт-метал (ТРГ-Ме) у температурному інтервалі 300–850 К. Композити ТРГ-Ме(Co, Ni) виготовлено методом відновлення катіонів металу у водному розчині тетрагідроборатом натрію. Структурно-фазовий склад композитів визначався за допомогою методів рентгенівської дифракції, скануючої електронної мікроскопії, Оже-та вторинної іонної мас-спектрометрії. Результати цих досліджень вказують на те, що метал у свіжовиготовлених композитах знаходиться, ймовірно, у зв'язаному стані у вигляді Ме-В та Ме-Н. Поступове нагрівання (до 850 К) або відпал (при 825 К) композитів ТРГ-Ме призводить до виникнення феромагнітних властивостей. Термоциклювання зразків ТРГ-Ме призводить до зменшення магнітної сприйнятливості, що спричиняється окисненням металічних частинок.