

THERMAL STABILITY OF NANOCOMPOSITE MATERIAL GRAPHITE-COBALT

Ludmila Vovchenko^{*1}, Ludmila Matzui¹, Mykola Zakharenko¹, Mykhailo Semen'ko¹,
Anatolij Brusilovetz²

*Kyiv National Taras Shevchenko University, Departments of ¹Physics and ²Chemistry,
Volodymyrska Str., 64, 01033 Kyiv, Ukraine*

Corresponding author e-mail address: vovch@univ.kiev.ua

Introduction

The method of graphite intercalation with a subsequent reduction of metal in the graphite intercalation compound (GIC) [1-2] is widely used recently in order to obtain the metals in nanodisperse state on graphite support. There are several modifications of this method. One of them is the reduction of metal salt by graphite intercalation compound C₈K. In this case the possibility to obtain metal particles both on the surface and in the bulk of graphite support is expected. The prepared "graphimets" contain "atomically distributed metal" between graphite layers and metal particles on graphite surface.

Experimental

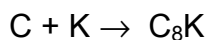
The method of graphite intercalation with a subsequent reduction of metal in GIC C₈K had been used in order to obtain the metals in nanodisperse state on graphite support. Graphite-Co powders were obtained by reduction of CoCl₂ compound to pure Co by C₈K intercalation compound.

C₈K compounds have been prepared using two different types of graphite: natural disperse graphite (Gr) (size of flakes is 50μm) and thermoexfoliated graphite (TEG) [3]. The prepared graphite-Co nanocomposites have been studied by the X-ray diffraction, scanning electron microscopy (SEM), Auger-spectroscopy and secondary ion-mass spectrometry (SIMS).

Results and Discussion

The preparation of graphite-Co powders may be described by the following chemical reactions:

a) Graphite intercalation by potassium according to the scheme:



The identity period of potassium intercalant layers was found to be equal to 5.33Å for the first stage of C₈K graphite compound [4].

b) The reaction of cobalt chloride reduction was performed in tetrahydrofuran (THF) medium.

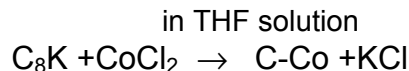


Fig.1 presents the X-ray diffraction patterns for the prepared specimens of composite materials (CMs). A series of additional reflections as compared to graphite that have been observed corresponds to intercalant layers with identity period l_c . The obtained Gr-Co CM was the GIC of the third stage with $l_{c3}=13,8\text{\AA}$ and distance between graphite layers that contain the layer of intercalant $d_i=6,9\text{\AA}$. The obtained TEG-Co CM was the GIC of mixed stages ($l_{c3}=13,8\text{\AA}$, $l_{cs}=11,0\text{\AA}$).

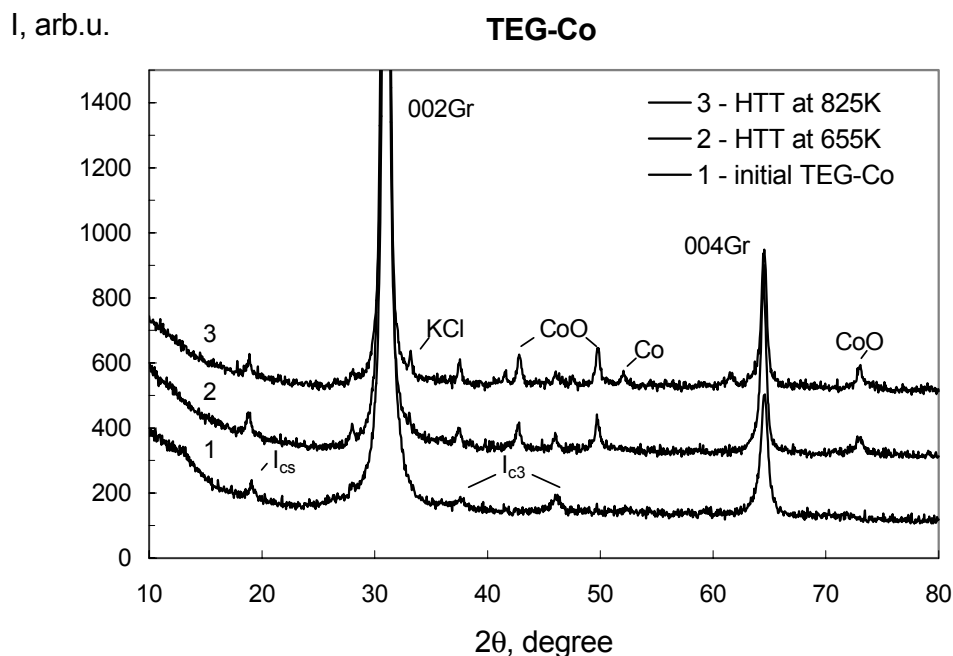
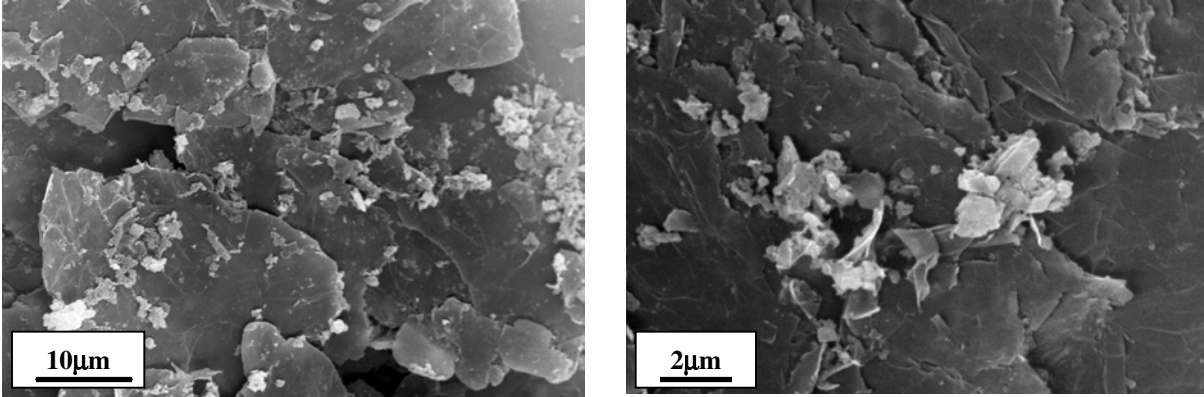


Figure 1. The X-ray diffraction patterns for graphite-Co specimens: 1- as-prepared TEG-Co; 2 – TEG-Co heat treated at $T=655\text{K}$, 40min.; 3 – TEG-Co heat treated at $T=825\text{K}$, 40min.

The intercalant layers may consist of Co, K and probably KCl and CoCl_2 . Partially these substances being formed are on the surface of graphite macro-planes. Co is oxidized and forms cobalt oxides. The data of electron microscopy studies of produced TEG-Co are presented in Fig.2. As it is seen from Fig.2, the TEG surface is covered by spherical particles (CoO with minimal size $\sim 80\text{nm}$) and flakes (probably CoCl_2 or KCl with size $\sim 700\text{nm}$). The presence of oxides is confirmed by the data of the Auger spectroscopy (Fig. 3). These data also prove the presence of low amount of CoCl_2 , which does not react with potassium in C_8K . Since no diffraction peaks corresponding to cobalt oxides were observed at the X-ray diffraction pattern for as-prepared TEG-Co (Fig.1, diagram 1), one can conclude the ultra-disperse state of Co oxide particles.



a)

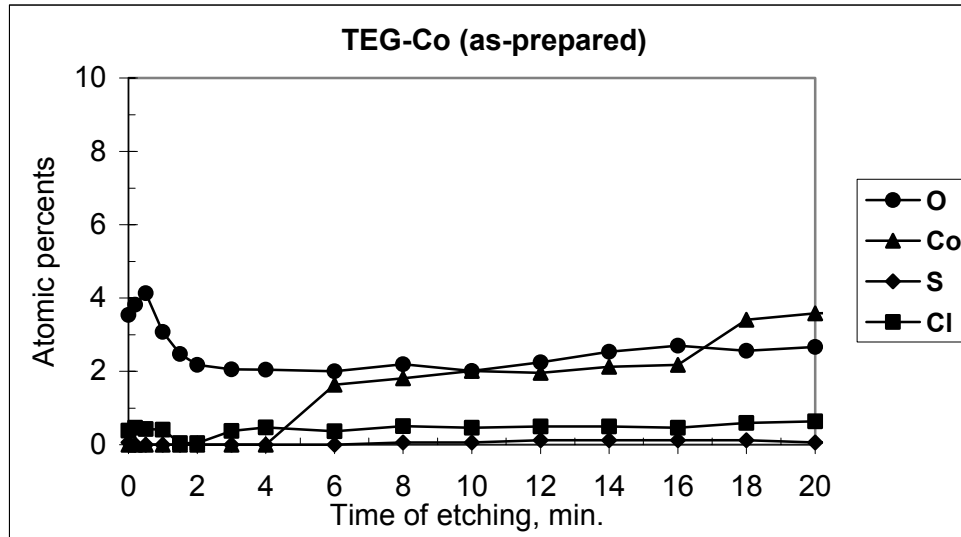
b)

Figure 2. SEM images of TEG-Co particles obtained through C_8K : a – as-prepared TEG-Co; b – TEG-Co heat treated at $T=825K$.

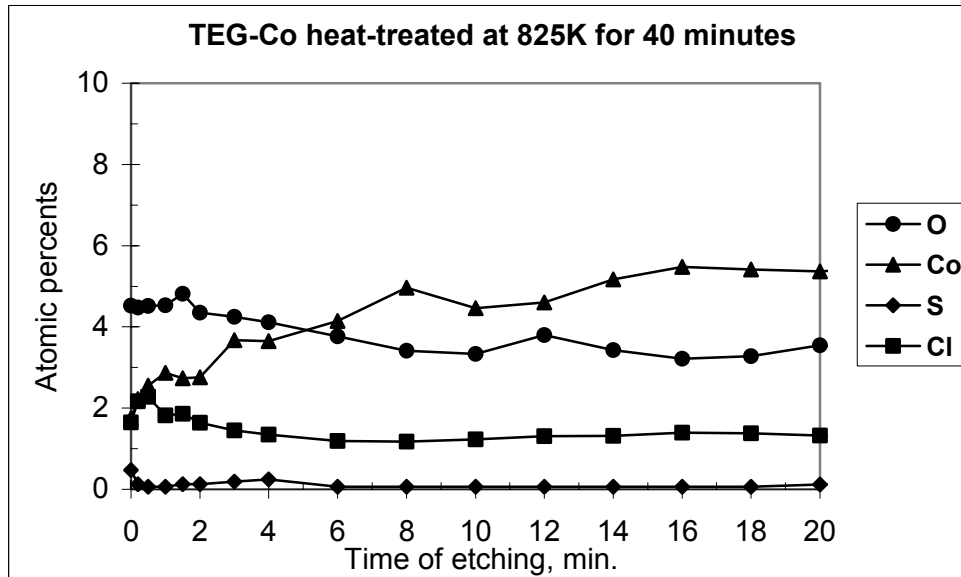
These assumptions concerning phase composition of graphite-Co powders are confirmed also by the data of secondary ion-mass spectrometry (SIMS) (Table 1).

Table 1: Yield of single-charged ions of elements and compounds (SIMS, normalized by C)

Mass	Elem./Compound	Gr-Co, as-prepared	TEG-Co, as-prepared	TEG-Co heat treated at $T=655K$	TEG-Co heat treated at $T=825K$
Positive ions					
1	H^+	1920	2120	1094	802
16	O^+	25	175	165	404
35	Cl^+		543	355	1124
39	K^+	191089	828000	496186	1095434
59	Co^+	78977	72100	75698	198457
71	CoC^+	82	139	242	264
94	$CoCl^+$	106	23	15	38
98	KCo^+	89	75	65	166
113	K_2Cl^+		51	9	70
118	Co_2^+	1111	383	351	875
75	CoO^+	351	248	304	1363
Negative ions					
1	H^-	8640	11400	40811	702
16	O^-	9429	14200	89862	11690
35	Cl^-	32509	10200	92020	16855
94	$CoCl^-$		3	0	6



a)



b)

Figure 3. The Auger spectroscopy data for the TEG-Co composite: a) as-prepared TEG-Co; b) – TEG-Co heat treated at $T=825\text{K}$; rate of etching – $5\text{\AA}/\text{min}$.

The studies of graphite-Co specimens after heat treatment at the temperature ranging from 300 to 850 K have been also performed. The data of the X-ray diffraction studies are presented in Fig.1(diagrams 2, 3). It was found that the phase transformations in graphite-Co powder occur at heating over 585K.

The analysis of the obtained results permits to conclude: the gradual deintercalation of graphite-Co intercalated compounds occurs at their heating up to 850K (diagrams 2, 3). The intensity of intercalant reflections decreases. The additional peaks corresponding to CoO oxides appear under heat treatment of produced TEG-Co CM up to $T=655\text{K}$

(diagram 2). This is caused by the segregation of CoO nanoscaled particles. Long-term heat treatment of TEG-Co powder at 825-850K leads to the increase of the intensity CoO peaks. Besides, Co atoms outcrop onto graphite surface. A fraction of them forms cobalt oxide, another form nanoscaled metallic particles. The X-ray pattern for the powder annealed at 825K contains the peaks of graphite, pure Co and Co oxides, and weak peaks of intercalant (diagr. 3). The presence of fine Co particles is indicated by the sharp increasing of magnetic susceptibility after heating the samples over 550 K. So, one can consider cobalt to be in the following states: (i) CoO phase on the graphite surface; (ii) nanoscaled Co particles on the graphite surface; (iii) separate atoms or 2D clusters between graphite layers. No continuous layers of Co exist in this material in contrast to GIC.

Conclusion

Thus, it was shown that the graphite-Co nanocomposite materials could be obtained through reduction of CoCl_2 by the intercalation compound C_8K . The performed investigations showed Co being both between graphite layers in a form of "atomically" distributed metal and on the surface of graphite support in a form of nanoscaled particles. A stage thermal treatment of the produced graphite-Co nanocomposite materials permits to shift the ratio of Co contents on the surface and between layers of graphite toward the increasing of Co content on the graphite surface.

References

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