

# Kinetics of phase transitions in highly oriented graphite intercalated with potassium

*I.F.Mikhailov, E.N.Zubarev, A.I.Mikhailov,  
V.V.Mamon, S.S.Borisova, S.V.Surovitskiy*

Department of Physics of Metals and Semiconductors, National Technical University "Kharkiv Polytechnic Institute", 2 Kyrpychova Str., 61002 Kharkiv, Ukraine

*Received May 7, 2020*

The kinetics of structural transformations of atomic-layered structures of highly oriented pyrographite intercalated with potassium ( $C_{60}K$ ,  $C_{36}K$ ,  $C_{24}K$ , and  $C_8K$ ) at  $T_{\text{HOPG}} = 300^\circ\text{C}$  has been studied by *in situ* XRD. The shape of the kinetic curves suggests a complex nature of the rearrangement of the structure of  $C_{24}K$  into  $C_{36}K$  and  $C_{48}K$ : first,  $C_{36}K$  is formed from  $C_{24}K$ , and then  $C_{48}K$ . The  $C_{60}K$  phase with a minimum potassium content is observed only at the final stage ( $t = 24$  h), when the remaining phases are practically not detected. Only the  $C_{60}K$  phase with the lowest potassium content is found to be structurally stable for 5 months.

**Keywords:** intercalation-deintercalation kinetics, high-oriented pyrolytic graphite, potassium, X-ray diffraction.

**Кінетика фазових переходів у високоорієнтованому графіті, інтеркальованому калієм.** *І.Ф.Михайлов, Ю.Н.Зубарев, А.І.Михайлов, В.В.Мамон, С.С.Борисова, С.В.Суrowицький.*

Кінетика структурних перетворень атомно-шаруватих структур високо-орієнтованого пірографіту, інтеркальованого калієм ( $C_{60}K$ ,  $C_{36}K$ ,  $C_{24}K$ , та  $C_8K$ ), при  $T_{\text{HOPG}} = 300^\circ\text{C}$ , досліджено методом рентгенівської дифракції *in situ*. Форма кінетичних кривих свідчить про складну природну перебудову структури  $C_{24}K$  на  $C_{36}K$  та  $C_{48}K$ : спочатку з  $C_{24}K$  утворюється  $C_{36}K$ , а потім  $C_{48}K$ . Фаза  $C_{60}K$  з мінімальним вмістом з'являється лише на завершальній стадії ( $t = 24$  год), коли інші фази практично не виявляються. Тільки фаза  $C_{60}K$  з найменшим вмістом калію виявилася структурно стабільною протягом 5 місяців.

Кинетику структурных превращений атомно-слоистых структур высокоориентированного пирографита, интеркалированного калием ( $C_{60}K$ ,  $C_{36}K$ ,  $C_{24}K$ , и  $C_8K$ ), при  $T_{\text{HOPG}} = 300^\circ\text{C}$ , исследована методом рентгеновской дифракции *in situ*. Форма кинетических кривых свидетельствует о сложной природе перестройки структуры  $C_{24}K$  в  $C_{36}K$  и  $C_{48}K$ : сначала из  $C_{24}K$  образуется  $C_{36}K$ , а затем  $C_{48}K$ . Фаза  $C_{60}K$  с минимальным содержанием калия наблюдается только на завершающей стадии ( $t = 24$  ч), когда остальные фазы практически не обнаруживаются. Только фаза  $C_{60}K$  с наименьшим содержанием калия оказалась структурно стабильной в течение 5 месяцев.

## 1. Introduction

Intercalated single crystals based on pyrographite and fullerene presents a new class of materials. In these materials, it is

possible to create layered structures with a mono-atomic layer thickness. This ensures the realization of quantum effects in thermal and electrical properties, as well as the specificity of monochromatization of X-ray

radiation and thermal neutrons. The first works devoted to the study of intercalation processes appeared in the 80s–90s of the last century [1–4]. In recent years, interest in these materials has increased, which is due to the prospects for use in many industries [5–9]. Work on the intercalation of highly oriented pyrographite is being carried out in the United States to create thermal neutron monochromators. In 2011, the first such monochromator was installed at a US research center at a thermal neutron source [10]. In these works, it was found that the most difficult problem is not the creation of an intercalated single crystal, but the degradation of structural characteristics, which is determined by the kinetics of the intercalation-deintercalation process. The kinetic characteristics of these processes have not yet been thoroughly studied. This makes it impossible to understand the physicochemical laws and to block the processes of degradation of the structures. A few studies carried out in this direction abroad [5, 9] are not able to establish either the order of reactions at each stage, nor their speed and activation energy. These problems can be solved only if a complex of structural methods is used [11, 12]. The use of these X-ray methods makes it possible to experimentally isolate the contribution of each process and to establish experimentally the limiting stages of the intercalation-deintercalation process. Blocking the degradation of the structure is possible only by external action on the kinetics of deintercalation under the control of the rate of three main processes: consumption of the metal source, escape of the metal outside the reaction volume, saturation of the carbon material with metal with the formation of a layered structure.

The aim of this work was to study the kinetics of deintercalation of atomic-layered structures of highly oriented pyrographite intercalated with potassium ( $C_{60}K$ ,  $C_{36}K$ ,  $C_{24}K$ , and  $C_8K$ ) by X-ray diffraction.

## 2. Experimental

The installation for intercalation of high-oriented pyrolytic graphite (HORG) consists of a quartz tube with a diameter of 20 mm and a length of 300 mm, welded on one side, a valve, two heating stoves, stove power supplies and temperature meters. The quartz tube is connected to the valve and sealed with a rubber seal. The valve together with a quartz tube is connected by means of a stainless tube to the VUP-5M

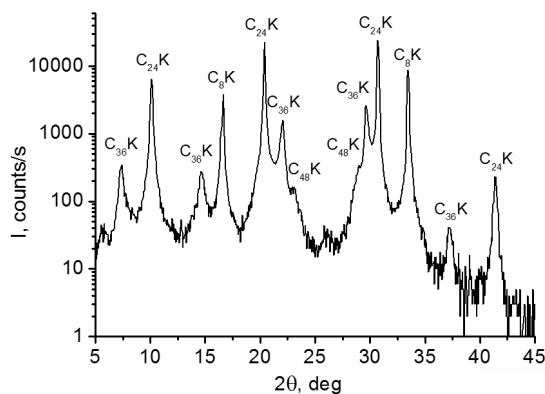


Fig. 1. Diffraction spectrum of a sample of HOPG intercalated with potassium in the initial state.

vacuum unit. Two stoves are made in the form of a separate removable block, which is put on the quartz tube. The temperature of each stove was measured using two chromel-alumel thermocouples. Metallic potassium was placed at the bottom of the quartz tube, and pyrolytic graphite was hung on a quartz rod inside the quartz tube. Potassium was heated by the lower stove and pyrographite — by the upper stove. To increase the potassium vapor pressure, a stainless steel beaker was placed above the sample.

This paper presents the results of a study of HOPG intercalated by potassium at a temperature  $T_{\text{HOPG}} = 300^\circ\text{C}$ . In this case, the temperature of the evaporated potassium was  $T_K = 235^\circ\text{C}$ .

The X-ray diffraction measurements were performed using a DRON-3M X-ray diffractometer in the radiation of the copper anode of the X-ray tube. Monochromatization of X-ray radiation ( $\text{Cu-K}\alpha$ ) was achieved using a graphite monochromator installed after the sample in front of the X-ray detector. All the diffraction spectra were registered sequentially one after another in the angular range  $1.0 \leq 2\theta \leq 50.0$  deg. The duration of each measurement was 25 min. kinetics of structural transformations during potassium deintercalation in highly oriented pyrographite under exposure in air at room temperature was studied by *in situ* XRD.

## 3. Results and discussion

The diffraction patterns of the samples of HOPG intercalated by potassium are shown in Figs. 1 and 3. In the initial state, the sample contains preferentially two

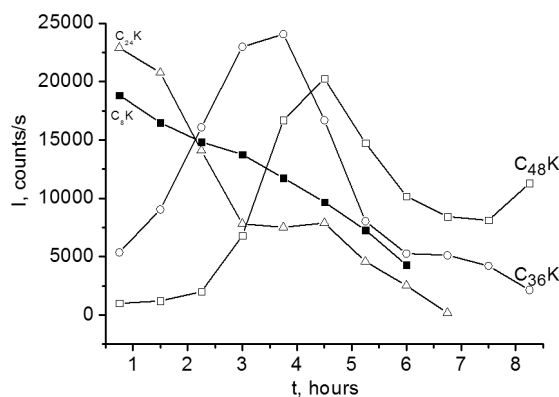


Fig. 2. Kinetic curves of the deintercalation process for different phases in HOPG intercalated with potassium.

phases with the highest potassium content,  $C_8K$  and  $C_{24}K$  (Fig. 1); the phases  $C_{36}K$  and  $C_{48}K$ , which are less rich in potassium, are practically not detected.

Fig. 2 shows the kinetic curves of changing the contents of all the phases registered. The  $C_8K$  content decreases with time according to a linear law characteristic of a zero-order reaction. The content of the  $C_{24}K$  phase decreases nonmonotonically with time, a characteristic inflection of the curve is observed at  $t = 4-5$  h. The reflections of  $C_{36}K$  and  $C_{48}K$  phases were too weak at the beginning of exposure; however, over time, their intensity increases, reaching a maximum value at  $t = 3.2$  h for  $C_{36}K$  and  $t = 4.5$  h for  $C_{48}K$ , and then decreases. The position of the maximum potassium content in the sample for these phases corresponds to the position of the inflection on the  $C_{24}K$  kinetic curve. The observed shape of the curves suggests a complex nature of the rearrangement of the structure of  $C_{24}K$  into  $C_{36}K$  and  $C_{48}K$ : first,  $C_{36}K$  is formed from  $C_{24}K$ , and then  $C_{48}K$ .

The  $C_{60}K$  phase with a minimum potassium content is observed only at the final stage ( $t = 24$  h), when the remaining phases are practically not detected (Fig. 3). However, this phase has a long-term temporal stability. Exposure of highly oriented graphite with the  $C_{60}K$  phase for 5 months does not lead to noticeable changes in the intensity of diffraction reflections of this phase, as well as to the appearance of reflections of other phases.

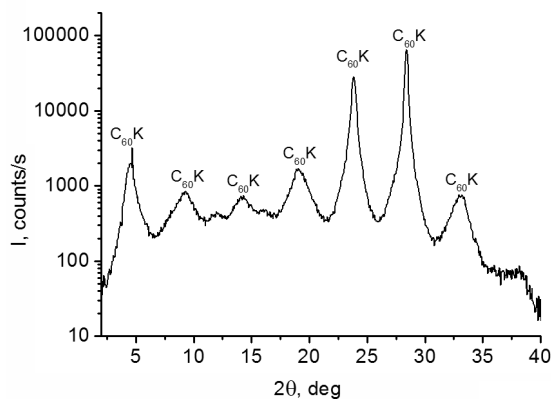


Fig. 3. Diffraction spectrum of a sample of HOPG intercalated with potassium after exposure in air for 5 months.

#### 4. Conclusion

During temporal exposure of highly oriented pyrographite intercalated with potassium, the sequence of deintercalation was experimentally established — a transition from phases with a high potassium content:  $C_8K$  and  $C_{24}K$  — to phases with a low potassium content:  $C_{36}K$ ,  $C_{48}$ , and  $C_{60}K$ . Only the  $C_{60}K$  phase with the lowest potassium content is structurally stable.

#### References

1. M.E.Misenheimer, H.Zabel, *Phys. Rev. B*, **27**, 1443 (1983).
2. S.A.Solin, N.Caswell, *J. Raman Spectrosc.*, **10**, 129 (1981).
3. V.A.Nalimova, M.El Gadi, D.Guerard et al., *Carbon*, **33**, 153 (1995).
4. Herold, M. El Gadi, J-F.Mareche, P.Lagrange, *Mol. Cryst. Liquid Cryst.*, **244**, 41 (1994).
5. Y.Li, Y.Lu, P.Adelheim et al., *Chem. Soc. Rev.*, **17**, (2019).
6. Jin Zhao, Xiaoxi Zou et al., *Adv. Funct. Mater.*, **26**, 8103 (2016).
7. J.Purewall, J.Brandon Keith et al., *J.Chem. Phys.*, **137**, 224704 (2012).
8. J.Liu, T.Yin, B.Tian et al., *Advan. Energy Mater.*, **9**, 22 (2019).
9. M.Chandesris, D.Caliste et al., *J. Phys. Chem. C*, **123**, 23711 (2019)
10. P.Courtois, C.Menthonnex, R.Hehn et al., *Nucl. Instrum. Meth. Phys. Res. A*, **634**, S37 (2011).
11. I.F.Mikhailov, A.A.Baturin, A.I.Mikhailov, L.P.Fomina, *Functional Materials*, **23**, 5 (2016).
12. A.I.Mikhailov, *Functional Materials*, **27**, 3 (2020).