In situ observation of staging in potassium-graphite intercalation compounds

R. Nishitani, Y. Uno, and H. Suematsu

Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

(Received 23 November 1982; revised manuscript received 14 February 1983)

Stage transformations in the potassium-graphite intercalation compound have been studied by *in situ* x-ray diffraction. A precise phase diagram has been determined for the stages up to 7. The stage dependence of $\Delta\mu(n)$, the stable range of a given stage n in chemical potential, is evaluated from the phase diagram and compared with the theoretical results for the eletrostatic model for staging. Time-dependent observation of the stage transformation reveals that only two phases of adjacent stages coexist throughout the process of the stage transformation so that the c-axis disorder is insignificant even in the transition region. The kinetics of the stage transformation is also discussed.

INTRODUCTION

The most remarkable property of graphite intercalation compounds (GIC's) is the stage structure, namely, the c-axis long-range order of intercalant layers. While many efforts have been made to investigate the stage and also the in-plane structures, as well as the electronic structure,[1-4] the fundamental problems associated with staging have not been sufficiently clarified; one is the origin of the long-range order, and the other is the dynamics of the stage-stage transformation. Recently Safran, and Safran and Hamman have calculated a phase diagram for stages of GIC's assuming the electrostatic interlayer interaction,[5,18] and Millman and Kirczenow have obtained an extended result by taking into account the separation energy to admit the intercalant into graphite layers.[6] Many experimental studies of the phase diagram have been described in the literatures[2,3,7-13] for alkaline-metal GIC's, the typical compounds of stage structure; but a detailed phase diagram up to higher stages has not been investigated, which can be compared with the recent theories. On the other hand, while the stage transformation has been interpreted on the basis of the Daumas-Herold model[14] [cf. Fig. 5(a)], the structural study of the dynamic process has not been investigated, except for a few cases such as Cs GIC[12] and Br_2 GIC.[2,15-17]

The purpose of this Communication is twofold: one, to determine a precise phase diagram for stages of the potassium (K) GIC's by *in situ* x-ray diffraction to elucidate the origin of staging; and, two, to investigate the time dependence of the stage transformation to discuss its dynamic process.

EXPERIMENTAL

The *in situ* x-ray diffraction measurements were carried out by setting a two-zone furnace with two small windows for x ray on a goniometer. Graphite samples [highly oriented pyrolytic graphite (HOPG): $\sim 4 \times 4 \times 0.5$ mm^3] and potassium metals were sealed in a Pyrex glass ampoule. X-ray diffraction through the ampoule was observed by the energy-dispersive method at a fixed diffraction angle. For this purpose were used an intensive white x-ray source with a rotating target (Cu) and a solid-state detector (SSD) with the energy resolution of 200 eV. A signal from the detector was stored in a microcomputer system through a multichannel pulse-height analyzer. This energy-dispersive method enables us not only to use a small aperture for the furnace, but also to get a time-dependent diffraction pattern in a short time.

RESULTS AND DISCUSSIONS

The stage transformation in the potassium GIC's was controlled by changing the temperature of potassium T_K, that is, the corresponding metal vapor pressure, while the graphite temperature T_g was held constant. Figure 1 shows the $(00l)$ diffraction patterns obtained thus, which correspond to stages 1 to 7. Figure 2 shows phase diagrams for three different graphite temperatures, 541, 485, and 387.5 °C. The figure demonstrates clearly some discrete steps in each of which a stage is stable. We have observed stable temperature (T_K) regions for stages up to 7 in the present study. However, it is difficult to obtain any stable temperature region for stages higher than 8 although we can distinguish the stages up to 13. The T_K width of the transition from stage n to $n \pm 1$ is not wider than 6 °C for $n \leq 7$. The stage transformation can be achieved reversibly with the hysteresis of about 8 °C except for the initial intercalation of a pristine graphite sample.

From the T_K region of stabilizing a stage, we can evaluate the stability of a stage n as the range of chemical potential $\Delta\mu(n)$. This is an important ex-
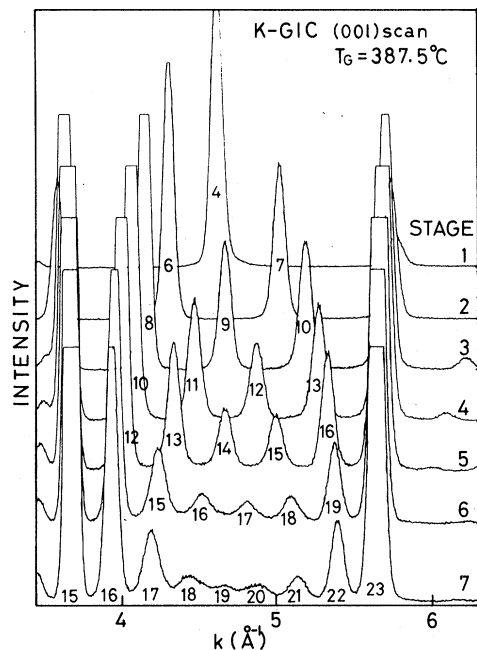
FIG. 1. X-ray $(00l)$ diffraction patterns for stage 1 to stage 7 in the potassium-graphite intercalation compound. The graphite temperature was held at $T_g = 387.5\,°C$. The temperatures of potassium metal T_K are 295, 264, 199, 186, 171, 168, and 166 °C for stages 1 to 7, respectively.

FIG. 2. Phase diagram of potassium-graphite intercalation compounds determined by in situ x-ray diffraction. The data were taken at the graphite temperatures of 387.5, 485, and 541 °C.

perimental parameter which yields information about the interaction responsible for staging. The experimental values for $\Delta\mu(n)$ are compared in Table I with the theoretical ones[18] calculated in the electrostatic interaction model for staging. The observed values $\Delta\mu(n)$ are hardly dependent on T_K within the temperature region of the present study. They are in good agreement with the theoretical result calculated for the ionicity of $f = \frac{1}{2}$. However, this result is in contrast to many electronic studies[19] which indicate that the ionicity for heavy alkaline-metal GIC's is very close to unity. The reason for this discrepancy is not clear at present. If we calculate the theoretical
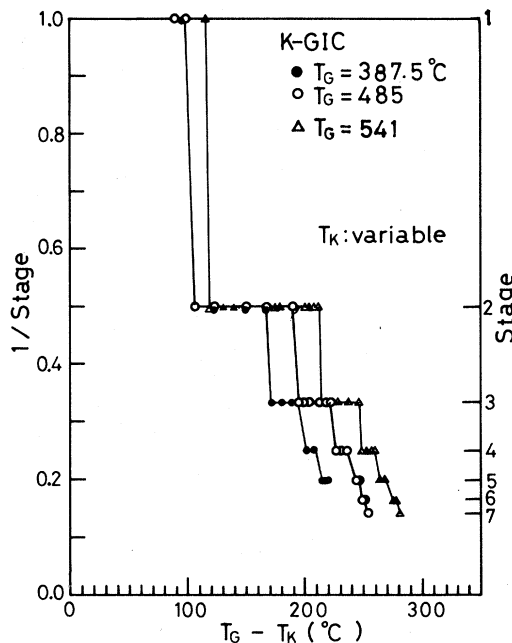
values at high temperatures, we could obtain the values smaller than those in Table I, and a larger ionicity than $\frac{1}{2}$.

In the case of the potassium GIC, we have observed no evidence of a microscopic mixture of two stages[20]; all the $(00l)$ diffraction peaks in the present study can be assigned to one or two diffraction series corresponding to one or two stages, respectively. According to the recent theories,[5,6,21] the weakly or non-screened potential of intercalant layers, such as the elastic one, may allow the formation of the microscopic mixtures of stages, while it cannot be allowed for the strongly screened potential. Therefore the present results suggest that the screened electrostatic

TABLE I. Range of stability of a stage. $\Delta\mu$ values given in eV.

	$\Delta\mu(2)$	$\Delta\mu(3)$	$\Delta\mu(4)$	$\Delta\mu(5)$	$\Delta\mu(6)$	
Experiment	0.150 ± 0.005	0.070 ± 0.005	0.038 ± 0.005	0.02 ± 0.005		$T_g = 387.5\,°C$
(Present work)	0.162	0.069	0.041	0.02	0.01 ± 0.005	$T_g = 485\,°C$
	0.168	0.070	0.040	0.02	0.018	$T_g = 541\,°C$
Theory[a] $f = \frac{1}{4}$		0.029	0.019	0.007		
$f = \frac{1}{2}$		0.069	0.036	0.024		
$f = 1$		0.176	0.072	0.044		

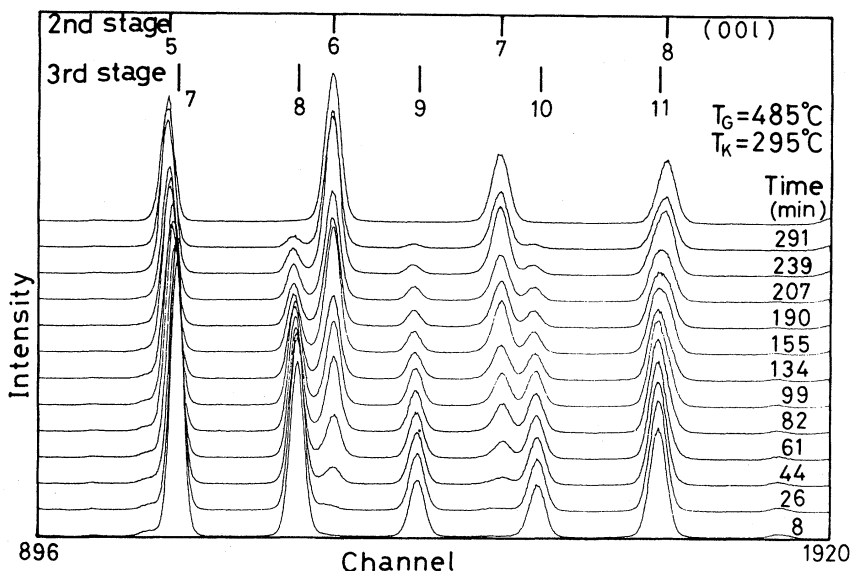[a]Reference 18. The calculation is made for $T = 0$ K.

FIG. 3. Time dependence of the $(00l)$ diffraction pattern in the stage transformation from stage 3 to stage 2. The patterns are shown as a function of time after changing the potassium temperature T_K from the equilibrium condition of stage 3 to the condition of stage 2.

interaction has an important role in the stage structure of potassium GIC's.

These results are in contrast to the cases of Br_2 and $FeCl_3$ GIC's in which the stable $\Delta\mu$ region of a stage is very narrow or disappears and the nonstaging or microscopic mixture can be observed.[16,22,23] Taking into account their small charge-transfer rate,[19,24] we can imagine that in these acceptor GIC's the elastic interaction is important for staging, rather than the electrostatic one. Thus those two cases of donor (K) and acceptor (Br_2, $FeCl_3$) GIC's seen to be extreme cases in staging mechanism.

Figure 3 shows the time dependence of the $(00l)$ diffraction pattern taken during the transition from stage 3 to stage 2 for $T_g = 485\,°C$. Starting from the pure stage 3, which is in equilibrium at $T_g - T_K = 195\,°C$, we have observed the growth of stage 2 as a function of time after changing T_K to that of stabilizing stage 2 ($T_g - T_K = 190\,°C$). The pattern at the bottom in Fig. 3 corresponds to the starting stage 3, and the top one to the final stage 2. In the transition region, we can see two sets of reflections of stages 3 and 2. With time, the reflection peaks for stage 2 grow and those for stage 3 decrease, in turn. The stage transformation was completed after 5 h. In the whole region of transition we have not observed any appreciable broadening of a reflection peak nor diffuse scattering along the c axis within the experimental accuracy. This fact indicates that a stage structure is kept undestroyed and two distinct stages coexist throughout the process of stage transformation [Fig. 5(c)].

Figure 4 shows the time dependences of the intensity of the stage-2 (006) reflection in the transition

region from stage 3 to stage 2 closed circles, $T_g = 387.5\,°C$; open circles, $T_g = 485\,°C$), and in the transition region from stage 1 to stage 2 (triangles, $T_g = 387.5\,°C$). The reflection of the growing stage seems to increase linearly with time after the start of the stage transformation until about 50% of a complete transformation. This behavior is suggestive of two-dimensional diffusion of potassium atoms in intercalant layers.

We can imagine a stage transformation by considering intercalant diffusion on the basis of the Daumas-Herold model. A stage-n structure has n different domains [Fig. 5(a)]. For instance, a stage-3 structure can transform into a stage-2 structure by intercalant diffusion indicated by arrows in Fig. 5(a).
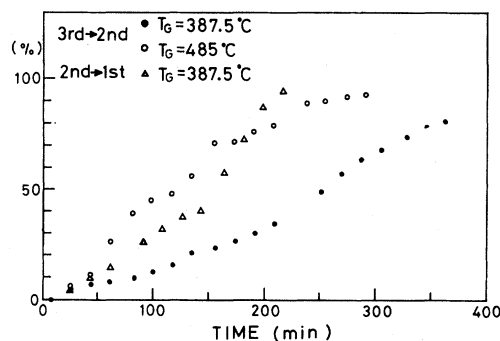

FIG. 4. Time dependences of the intensity of (006) reflection for stage 2 in the stage transformation from stage 3 to stage 2 (closed circles, $T_g = 387.5\,°C$; open circles, $T_g = 485\,°C$) and in the stage transformation from stage 1 to stage 2 (triangles, $T_g = 387.5\,°C$).
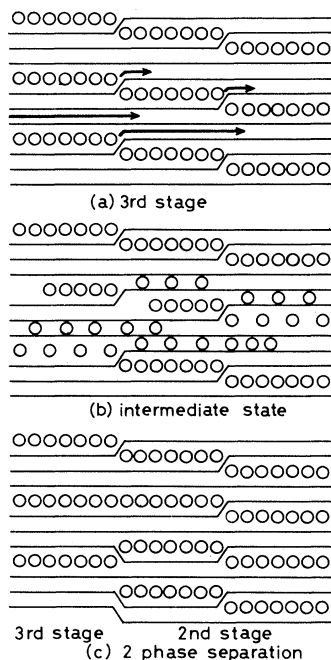
FIG. 5. (a) Dauman-Herold model for stage 3. (b) Possible intermediate structure in the stage transformation from stage 3 to stage 2. (c) Two-stage separation in the transition region from stage 3 to stage 2.

In this transformation, we are forced to consider an intermediate state [Fig. 5(b)] in which intercalants are passing through the phase boundary region to settle the proper domains so that the c-axis disorder should occur more or less. However, the fact is that no appreciable evidence of the intermediate state has been observed during the stage transformation.

Therefore we can say that in the stage transformation the phase boundary region should be small compared with the remaining well-staged regions, or otherwise the diffusion or intercalants be very rapid in the boundary region compared with their dwelling period at the proper domains.

SUMMARY

The stage transformations in the potassium GIC have been investigated by *in situ* x-ray diffraction. The precise phase diagrams for stages up to 7 have been determined for various graphite temperatures. Only pure stage structures have been observed. The stage dependence of $\Delta\mu(n)$ evaluated from the phase diagrams and the disappearance of the microscopic stage mixture are consistent with the theoretical results for the screened electrostatic interaction model. In the transition region from stage n to $n \pm 1$, only two phases of two stages n and $n-1$ (or $n+1$) coexist without c-axis disorder. This shows that the disordered region associated with the stage transformation should be very small compared with the well-staged region. The region of a growing stage seems to increase in proportion to time in the initial period of the stage transformation, which is suggestive of two-dimensional diffusion of potassium atoms.

[1] *Proceedings of the Second Conference on Intercalation Compounds of Graphite, Provincetown, Massachusetts, May 19—23, 1980,* edited by F. Lincoln Vogel [Synth. Met. 2 and 3 (1980)].

[2] M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. 30, 139 (1981).

[3] S. A. Solin, Adv. Chem. Phys. 49, 455 (1982).

[4] G. R. Hennig, Prog. Inorg. Chem. 1, 125 (1959).

[5] S. A. Safran, Phys. Rev. Lett. 44, 937 (1980).

[6] S. E. Millman and G. Kirczenow, Phys. Rev. B 26, 2310 (1982).

[7] A. Herold, Bull. Soc. Chim. Fr., 999 (1955).

[8] F. J. Salzano and S. Aronson, J. Inorg. Nucl. Chem. 26, 1456 (1964).

[9] D. E. Nixon and G. S. Parry, J. Phys. D 1, 291 (1968).

[10] B. Carton and A. Herold, Bull. Soc. Chim. Fr. 4, 1337 (1972).

[11] C. Underhill, T. Krapchev, and M. S. Dresselhaus, Synth. Met. 2, 47 (1980).

[12] N. Caswell, Phys. Rev. B 12, 6308 (1980).

[13] A. Herold, in *Physics and Chemistry of Materials with Layered Structures,* edited by F. Lévy (Reidel, Dordrecht, 1979), Vol. 6, p. 323.

[14] N. Daumas and A. Herold, C. R. Acad. Sci. Ser. C 268, 273 (1969).

[15] M. B. Dowell and D. S. Badorrek, Carbon 16, 248 (1978).

[16] T. Sasa, Y. Takahashi, and T. Mukaibo, Carbon 9, 407 (1971).

[17] K. K. Bardhan, J. C. Wu, J. S. Culik, S. A. Anderson, and D. D. L. Chung, Synth. Met. 2, 57 (1980).

[18] S. A. Safran and D. R. Hamann, Phys. Rev. B 23, 565 (1981).

[19] See Tables 4.7 and 4.14 in Ref. 2.

[20] "A microscopic mixture of two stages" refers to a disordered mixture of two stages and also to an ordered periodic structure of alternating two stages (the latter of which is called *nonpure* stage by Safran and Hamann; see Ref. 21).

[21] S. A. Safran and D. R. Hamann, Phys. Rev. B 22, 606 (1980).

[22] J. M. Thomas, G. R. Millward, R. F. Schlögl, and H. P. Boehm, Mater. Res. Bull. 15, 671 (1980).

[23] J. G. Hooley and M. Bartlett, Carbon 5, 417 (1967).

[24] S. Tanuma, H. Suematsu, K. Higuchi, R. Inada, and Y. Ōnuki, in *The Application of High Magnetic Fields in Semiconductor Physics,* edited by J. S. Ryan (Clarendon, Oxford, 1978), p. 85.