

# Deintercalation and Thermal Stability of Na-graphite Intercalation Compounds

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(Received January 8, 2001; accepted March 2, 2001)

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## Abstract

Na alloyed graphite intercalation compounds with stage 1 and 2 were synthesized using the high temperature and pressure technique. Thermal stability and staging transitions of the compounds were investigated depending on heating rates. The thermal stability and temperature dependence of the deintercalation compounds were characterized using differential scanning calorimeter (DSC) analyzer. Enthalpy of formations were confirmed at temperatures between 25 and 500°C, depending on the various heating rates. The structure changes of Na alloyed graphite compounds during the deintercalation reaction of sodium ions and interlayer spaces of the graphite were identified by X-ray diffraction (XRD). Diffractograms of stages with non-integral (00 $l$ ) values were obtained in the thermal decomposition process, and stacking disorder defects and random stage modes were observed. The average value of the interlayer C-C bond lengths were found approximately 2.12 Å and 1.23 Å from the diffractions. Based on the stage transition, the degree of the deintercalation has a inverse-linear relationship against the heating rate.

**Keywords :** Na-graphite Intercalation Compounds, Thermal Stability, Stage Transition, DSC, Enthalpy of Formation, XRD, C-C Bond Length

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## 1. Introduction

A great deal of attention has been given to the preparation of the graphite intercalation compounds (GICs), which were formed by the insertion of atomic or molecular layers of guest chemical species, called as intercalants, between layers of the host material. The stability of the graphite intercalation compounds is a crucial factor in the practical industrial and space or aircraft application [1]. Many theoretical studies on the stability have been reported dealing with the mechanism of staging and disorders of stage [2-4].

Generally, the intercalation reaction occurs relatively smoothly when graphite intercalation compounds nothing, but the alkali metal graphite intercalation compounds with poor stability. Among the GICs with alkali metal intercalants, Na-graphite compounds have been recognized to be significant because they are thermodynamically less stable than the K-, Rb-, and Ce- compounds [5-7]. Asher [7] reported the lamellar compound of sodium and graphite having an ideal formula  $C_{64}Na$ , in which sodium was intercalated in every eighth interplanar gap appeared to be analogous to the K-, Rb-, and Ce-graphite lamellar compounds. Blash *et al.* [8] synthesized the GICs such as  $C_2Na$  and  $C_3Na$  with sodium at  $T=450^\circ C$  and  $P=15\sim 50$  kbar, thereby indicating complete interaction of sodium with graphite, and refuted the notion concerning the impossibility

of formation of Na-GICs of low stages. The unusual sodium behavior in the intercalation with graphite had been explained by the thermodynamic instability of GICs at the synthesis temperature [9]. According to previous report, Udod *et al.* [10] have suggested that the limiting composition of the high pressure phase of Na-GICs at 40 kbar is  $Na_2C$  having a two-layer package of intercalant. It was established that high pressure treatments do not lead to a monolayer structure. However, no detailed studies of the deintercalation behavior of the Na-GICs have been reported at present. In this work, Na-GICs of low stages were synthesized using natural graphite and investigated the deintercalation and thermal stability depending on the heating rates.

## 2. Experimental

Natural graphite flakes (Sangjin, Korea) with a size between 100 and 200 mesh (approx. 0.149~0.074 mm), were used as a starting host material. They were purified by alkali melting method as one of the chemical treatment such as  $K_2CO_3$  or  $Na_2CO_3$ . The carbon content obtained from elemental analysis was  $98.08 \pm 1.15\%$ . The results of elemental analysis are listed in Table 1. As an intercalant, we used sodium in form of metal (Aldrich Chemicals, Inc., U.S.A.) and controlling the reaction atmosphere gas as Ar with the

Table 1. Elemental analysis of the purified starting natural graphite

Elemental contents (%)	C	H	N	O	S
Sangjin	98.08( $\pm$ 1.01)	0.32( $\pm$ 0.01)	0.05	0.42( $\pm$ 0.01)	0.00

purity of 99.999%. Na-GICs were synthesized by the chemical method under temperature and pressure with sodium metal and natural graphite. Thirty percent of sodium metal was put in stainless steel container. The synthesis has been performed at the temperature between 650 and 700°C, under the pressure of *ca.* 350~400 kg/cm<sup>2</sup> and under the argon atmosphere for 18~20 hours. The thermal stability, stage transition and temperature dependence of the deintercalation of the Na-GICs were investigated depending on various heating rates.

A Differential Scanning Calorimeter (DSC) analyzer (Netzsch, Germany) has been used to conform the thermal stability, temperature dependence, and reactivity under N<sub>2</sub> of the Na-graphite intercalation compounds. For the measurement, 0.21~0.25 g of GICs were weighed in dry box. Al<sub>2</sub>O<sub>3</sub> of *ca.* 0.2 g was used as a standard material and a Pt crucible was used for the reaction. Enthalpy of formation were confirmed at temperatures between 25 and 500°C, depending on the various heating rates, 1, 5, 10, 15, 20 and 25°C/min. The enthalpy and entropy were calculated by using Netzsch Instrument software (SW/xxx/65x.01). The structural changes of Na-GICs during the deintercalation of Na ions and the interlayer spaces of the graphites were identified by XRD. In the X-ray diffraction analysis, we can observe more reflection peaks for most graphite intercalation compounds than during intercalation that were obtained during the deintercalation process. For the study the structural change of the graphite deintercalation compounds (GDICs), the Debye-Scherrer camera with an ISO-DEBYEFLEX 3000 generator (Rich. Seifert & Co) was used for the XRD measurements. Cu K $\alpha$  radiation was used an incident beam. Each substance obtained after the intercalation and deintercalation reactions were filled in a capillary with the diameter of 0.5 mm $\Phi$  as dense as possible so that the texture phenomena can't occur. Each sample prepared in such method was filmed with Debye-scherrer camera under the condition of 45 kV and 40 mA for 7~8 hours. The films obtained in this way were interpreted with analyzer.

### 3. Results and Discussion

Alkali metals are intercalated into the graphite interlayer spacings with formation of electron donor-type intercalation compounds. It is characteristics of the intercalation compounds to form residual compounds when they are decomposed spontaneously in the air or oxidized electrochemically

with some parts of the intercalants remaining in the interlayer spacings [4, 11-13]. Because the vapour pressure of sodium is relatively higher than that of other alkali metals such as K, Rb, Ce, the properties of the graphite intercalation compounds with sodium are quite different. The thermal stability and the deintercalation of the Na-GICs for stage 1 and 2 were characterized using DSC to temperature of 500°C. Enthalpy and entropy of formations were calculated by the confirmation of the deintercalation and thermodynamic exothermic reactions. Fig. 1 shows the enthalpy of formation versus heating rate. Fig. 1(a) shows the biggest absolute value for the enthalpy of formation of -681.35 J/g. This value was formed by the heating rate of 1°C/min at the smallest temperature ranges between 219.9 and 279.9°C. Fig. 1(f) shows the smallest absolute value of -166.63 J/g formed by the heating rate of 25°C/min at the biggest temperature ranges between 91.4 and 447.1°C. In Table 2, the enthalpy and entropy of formation corresponding to each temperatures are listed depending on the heating rates. Based on the results, the enthalpy of formation represents the dependence of the heating rates.

The temperature and pressure are the decisive factors in the intercalation and deintercalation process. The structural changes occurring during the thermal decomposition process of the Na-GICs can be detected by X-ray diffraction device with the results shown in Fig. 2. The perfect compound for stage 1 could not be found in the Na-GICs. A weak diffraction peak could be observed on the (00 $l$ ) interference for the stage 2. The observed compound of NaC<sub>64</sub> for the stages were reported by previous workers [7, 14]. Metrot *et al.* [15] gave sorption isotherms for the soft and hard carbons. The sodium uptake in soft carbon was found to be mainly due to intercalation. The amount of sodium decreased as the treatment temperature of the cokes increased. In this study, we could obtained blue and red Na-GICs for stage 1 and 2. The deintercalation for stage 1~5 compounds could be found by the temperature of 500°C, in which the stage 3 was a main structure in the deintercalation compounds. In the case of the compounds with the heating rate of 5 and 10°C/min, a weak peak was observed on the lower stage (stage 1 or 2) and stage 4 and 5, but a peak of original graphite was strongly revealed. For the heating rate of 15 and 20°C/min, the stage 5, 6 and 8 were main structures, in which the peak of original graphite was stronger than other cases. And finally, in the case of the compounds with the heating rate of 25°C/min, a very weak peak was observed on the lower stage and stage 5, 6 and 8. The kinetics of final residue compounds characterized by the relation of the deintercalation temperature of 500°C.

During the thermal decomposition process, diffractograms of stages with non-integral (00 $l$ ) values were obtained, characteristic of stacking disorder defects and random stage modes in the Na-GDICs. Table 3 shows the average values of  $d_c$  for the each stage found at the end of each heating rate

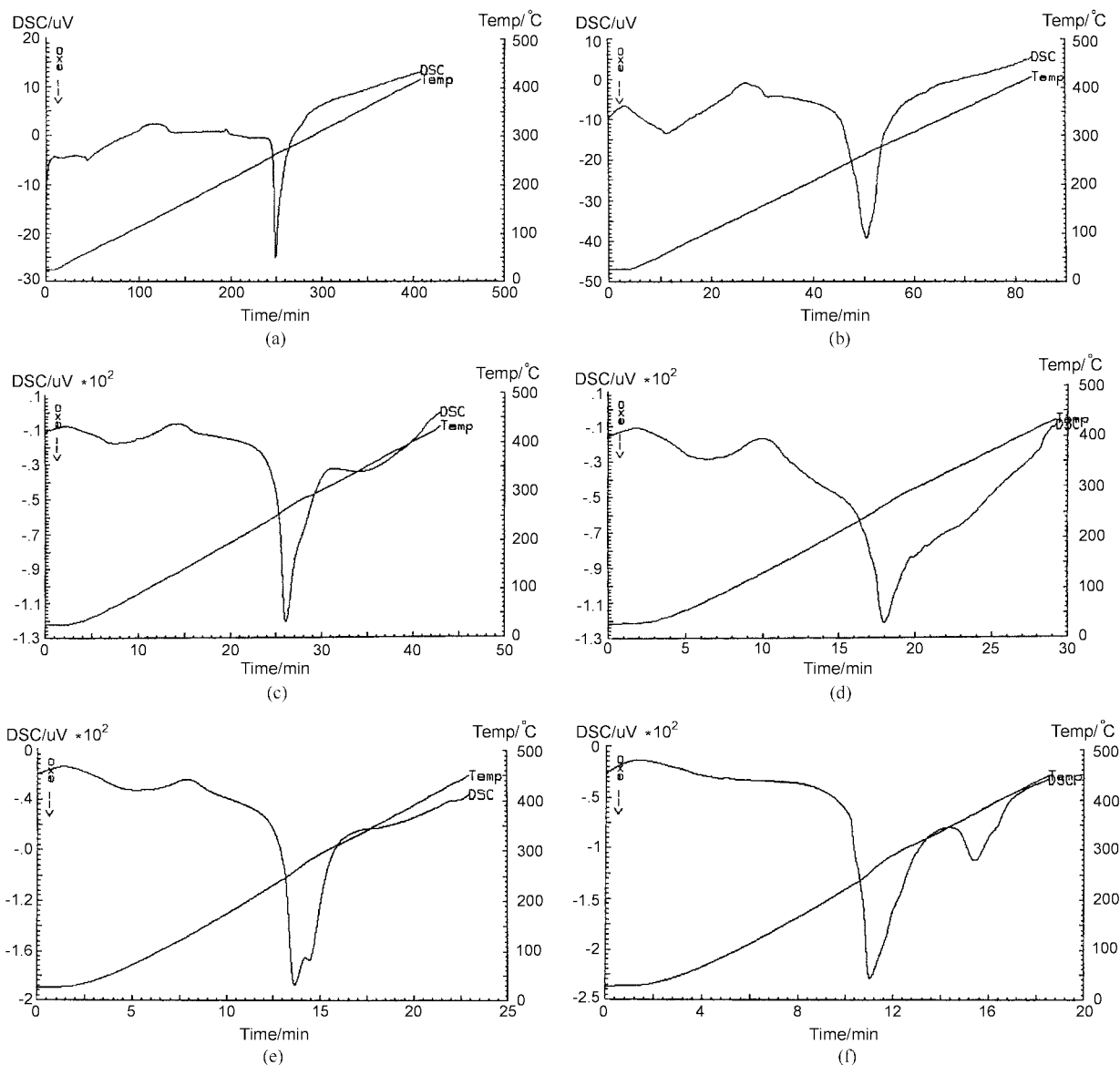


Fig. 1. Differential scanning calorimetric analysis of Na-GDICs showing the endothermic reaction on various heating rates (a) 1°C/min (b) 5°C/min (c) 10°C/min (d) 15°C/min (e) 20°C/min (f) 25°C/min.

Table 2. Thermodynamic data of Na-graphite intercalation compounds

Na-GDIC <sub>Heating rate</sub>	Temperature range (°C)	$\Delta H$ (J · g <sup>-1</sup> )	$\Delta S$ (J · g <sup>-1</sup> · K <sup>-1</sup> )	Degree of deintercalation [-ln(1-X)]
Na-GDIC <sub>1°C/min</sub>	219.9~279.9(249)	-681.35	-1.305	—
Na-GDIC <sub>5°C/min</sub>	140.7~349.9(245)	-526.80	-1.017	1.31
Na-GDIC <sub>10°C/min</sub>	138.4~420.2(279)	-377.61	-0.684	0.96
Na-GDIC <sub>15°C/min</sub>	135.9~422.4(279)	-361.95	-0.656	0.62
Na-GDIC <sub>20°C/min</sub>	135.3~430.3(282)	-169.77	-0.306	0.37
Na-GDIC <sub>25°C/min</sub>	91.04~447.1(273)	-166.63	-0.305	0.26

※ ( ) : average temperature for  $\Delta S$  calculation

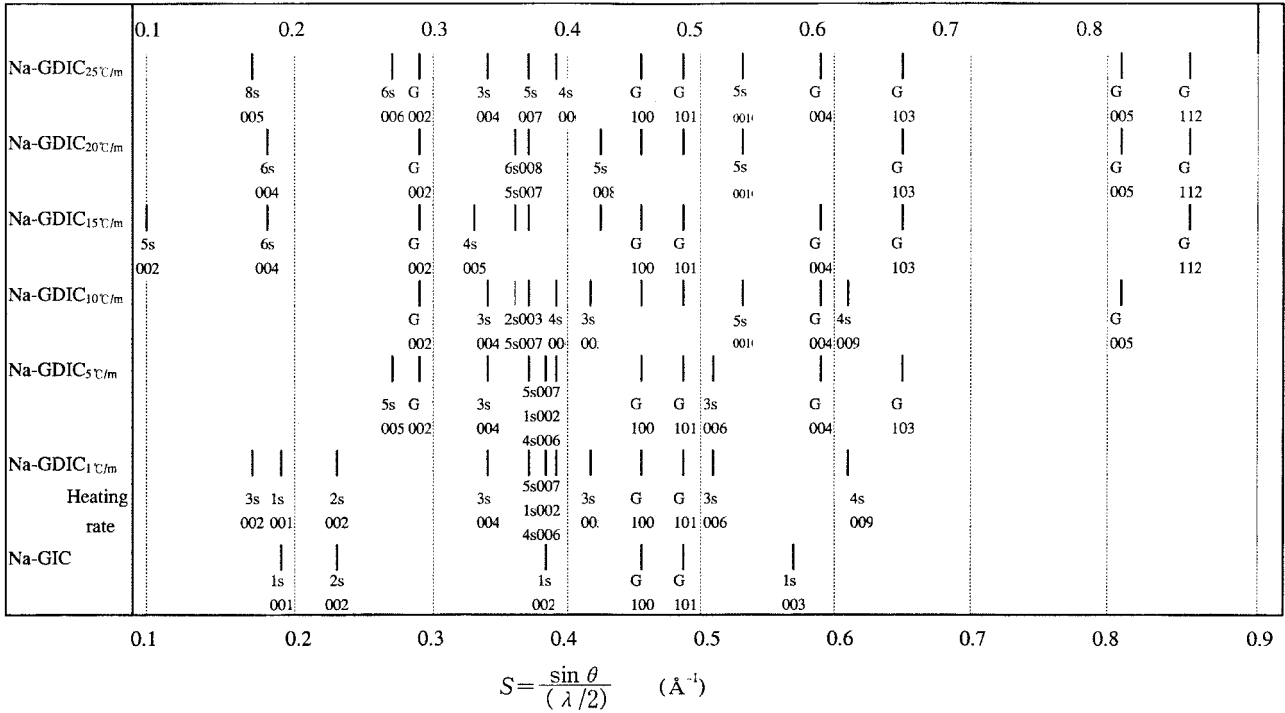


Fig. 2. X-ray diffraction for the deintercalation of Na-Graphite intercalation compounds by heating rates.

\*1s: stage 1, 2s: stage 2, 3s: stage 3....., G: graphite

Table 3. Average  $d_c$  values for the stages, as calculated from the 00 $l$  lines in the diffractograms and average interlayer C-C distances

	Average $d_c$ for the stages (Å)								$d_{c-c}$
	1	2	3	4	5	6	7	8	
Na-GIC	5.20	8.56							1.416
Na-GDIC <sub>1°C/min</sub>	5.21	8.55	11.90	<i>15.24</i>					1.414
Na-GDIC <sub>5°C/min</sub>			11.91	15.25	18.59				1.418
Na-GDIC <sub>10°C/min</sub>		8.56	11.90	15.25	18.60				1.419
Na-GDIC <sub>15°C/min</sub>				15.26	18.61	<i>21.94</i>			1.422
Na-GDIC <sub>20°C/min</sub>					18.61	<i>21.96</i>			1.420
Na-GDIC <sub>25°C/min</sub>			<i>11.90</i>	15.24	18.61	<i>21.94</i>		28.66	1.420

\*Values in *italics* were determined from single 00 $l$  diffractions and are therefore not averages

up to the formation of deintercalated compounds. This parameter is calculated using the expression

$$d_c = \left[ \sum_{i=1}^n d_i \cdot l_i \cdot \tan \theta_i \right] / \left[ \sum_{i=1}^n \tan \theta_i \right]$$

where  $n$  is the number of (00 $l$ ) lines relative to each stage in the given diffractogram and where the statistical weight of each value of  $d_i$  is taken as proportionally inverse to the uncertainty in the corresponding value of  $\theta_i$ .

It is also possible to obtain  $d_{c-c}$  from the proposed method [4]. The average value of the interlayer C-C bond lengths, from the reflexions at approximately 2.12 Å and

1.23 Å that are found in all the diffractograms, and which are both independent of the interlayer distance and only depend on the C-C bond lengths. The values thus calculated are also given in Table 3.

Based on the stage transitions by XRD, the kinetics of the deintercalation of Na-GICs were studied for heating rates between 1 and 25°C/min, and degree of deintercalation. On the assumption that the deintercalation is heating rate-controlled, the degree of the deintercalation follows a linear relationship. Therefore, the degree of the non-deintercalation ( $X$ ) and deintercalation ( $-\ln(1-X)$ ) are listed for the heating rates in Table 2 [2]. This relation indicates that the deintercalation is heating rate-controlled. The degree of the deinterca-

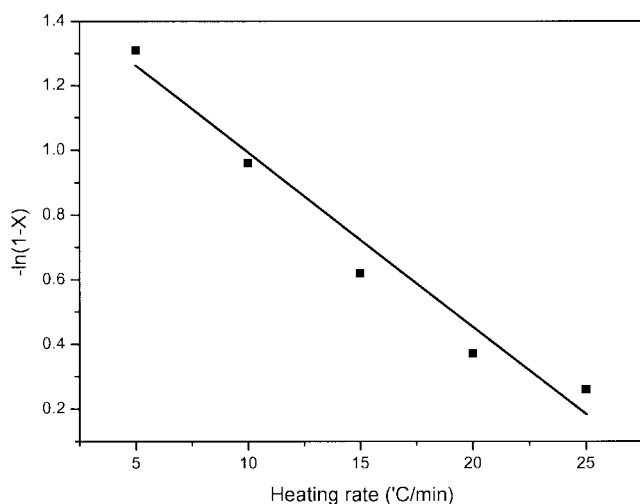


Fig. 3. Kinetic formation for heating rate-controlled deintercalation reaction of Na-GDICs.

lation has a inverse-linear relationship against the heating rate, as plotted in Fig. 3. The deintercalation reaction constant (K) calculated from this relationship is proposed to be  $5.8 \times 10^{-2}/\text{min}$ .

#### 4. Conclusion

In the present study, the Na-GICs were synthesized with stage 1 and 2 using the high temperature and pressure technique. This paper presents experimental results of the deintercalation reaction and thermal stability depending on the heating rates in the Na-GICs. From the DSC result, entropy of formation could be calculated through the confirmation of the deintercalation and thermodynamic exothermic reactions depending on the various heating rates. The enthalpy and entropy of formation represents that the values are dependent upon the heating rates. The structural changes of Na-GDICs depending on the heating rates were identified by XRD. During the thermal decomposition process, diffractograms of stages with non-integral (00l) values were obtained, characteristics of stacking disorder, defects, and

random stage modes. The average value of the interlayer C-C bond lengths, from the diffractions at approximately 2.12 Å and 1.23 Å that are found in all the diffractograms. The kinetics of final residue compounds characterized by the relation of the deintercalation temperature, and the heating rates. Based on the stage transition, the degree of the deintercalation has a inverse-linear relationship against the heating rate. The deintercalation constant is proposed to be  $5.8 \times 10^{-2}/\text{min}$ .

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