Deintercalation of Na-graphite intercalation compounds and their thermal stability

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1. Introduction

A great deal of attention has been given to the preparation of the graphite intercalation compounds(GICs) formed by the insertion of atomic or molecular layers of guest chemical species, called the intercalate, between layers of a host material. The stability of the GICs is a crucial factor in the practical industrial and space or aircraft application of these materials[1]. Many theoretical studies on the stability have been reported dealing with the mechanism and kinetics of the intercalations and the staging transitions concerning with structural staging mechanism and stage disorders[2,3].

Asher[4] reported the lamellar compound of sodium and graphite having an ideal formular $C_{64}Na$ in which sodium was intercalated in every eighth interplanar gap appeared to be analogous to the K-, Rb-, and Cs-graphite lamellar compounds. Belash et al.[5] synthesized the GICs with sodium C_2Na and C_3Na at T=450℃ and P=15-50 kbar, thereby indicating complete interaction of sodium with graphite, and refuted the notion concerning the impossibility of formation of Na-GICs of low stages. Recently, Udod et al.[6] have suggested that the limiting composition of the high pressure phase of Na-GICs at 40 kbar is NaC_2 having a two-layer package of intercalate. However, no detailed studies of the deintercalation behavior of the Na-GICs have been reported at present. In this work, we have synthesized Na-GICs using natural graphite, and investigated the deintercalation reaction and thermal stability depending on the heating rates.

2. Experimental

Natural graphite flakes(Sangjin, Korea) with a size between 100 and 200 mesh(approx. 0.149-0.074mm) were used as a starting host material. As an intercalant, sodium was used in form of metal. The Na-GICs were synthesized by the chemical method using high temperature and pressure in a stainless steel at temperatures between 650 and 700℃ at approximately 45 kbar for the reaction of sodium and graphite.

The thermal stability and the temperature dependence of the deintercalation compounds were characterized using differential scanning calorimeter(DSC) analyzer(Netzsch, Germany). Enthalpy formations were confirmed at temperatures between 25 and 500℃ depending on the various heating rates, 1, 5, 10, 15, 20 and 25 ℃/min. The structure changes of Na-GICs during the deintercalation reaction of Na ions and the interlayer spaces of the graphites were identified by XRD.

3. Results and discussion

The thermal stability and deintercalation reaction of the Na-GICs for stage 1 and 2 were characterized using DSC to temperature of 500℃. Enthalpy and entropy formations were calculated by confirming of the deintercalation and thermodynamic exothermic reactions depending on the various heating rates, 1, 5, 10, 15, 20 and 25℃/min. Table 1 shows the enthalpy formations versus various heating rates. Table 1(a) shows the biggest absolute value for the enthalpy formation of -681.35 J/g. This value was formed by the heating rate of 1℃/min at the smallest temperature ranges between 219.9 and 279.9℃. Table 1(f) shows the smallest absolute value of -166.63 J/g formed by the heating rate of 25℃/min at the biggest temperature ranges between 91.4 and 447.1℃.

The structure changes of Na-GICs depending on the heating rates were identified XRD in Fig. 1. 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_{64} for the stages were reported by previous workers[4,7]. In this study, we could obtained blue and red Na-GICs for stage 1 and 2. Deintercalation compound for stage 1-5 could be found by the deintercation process of the compounds with the heating rates of 1℃/min to the temperature of 500℃, 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℃/min, a weak peak was observed on the lower stage and stage 4 and 5, but a peak of original graphite was revealed strongly. For the heating rate of 15 and 20℃ /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℃/min, a very weak peak was observed on the lower stage and stage 5, 6 and 8, but a peak of original graphite was revealed strongly. As compared with the finally residue compounds, we can assume that the kinetics are related to the heating rates to the deintercalation temperature of 500℃.

4. Conclusion

In the present study, we have synthesized Na-GICs 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 DSC, entropy formations could be calculated by confirming of the deintercalation and thremodynamic exothermic reactions depending on the various heating rates. The structure changes of Na-GDICs depending on the heating rates were identified XRD.

Reference

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Table 1. Thermodynamic data of Na-graphite deintercalation compounds

$Na\text{-}GDIC_{Heating\ rate}$	Temperature range(℃)	ΔH ($J \cdot g^{-1}$)	ΔS ($J \cdot g^{-1} \cdot K^{-1}$)
(a)$Na\text{-}GDIC_{1℃/min}$	219.9~279.9	-681.35	-1.305
(b)$Na\text{-}GDIC_{5℃/min}$	140.7~349.9	-526.80	-1.017
(c)$Na\text{-}GDIC_{10℃/min}$	138.4~420.2	-377.61	-0.684
(d)$Na\text{-}GDIC_{15℃/min}$	135.9~422.4	-361.95	-0.656
(e)$Na\text{-}GDIC_{20℃/min}$	135.3~430.3	-169.77	-0.306
(f)$Na\text{-}GDIC_{25℃/min}$	91.04~447.1	-166.63	-0.305

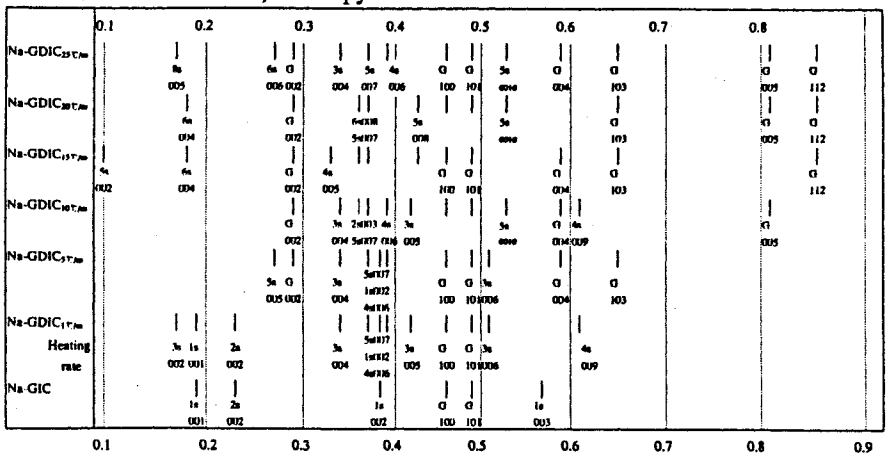

Figure 1. X-ray reflection for the deintercalation of Na-Graphite intercalation compounds by heating rates. * 1s : stage 1, 2s : stage 2, 3s : stage 3....., G : graphite

$S = \frac{\sin\theta}{(\lambda/2)}$