

EFFECT OF La AND/OR B LOADING AND HEAT TREATMENT ON STRUCTURAL CHANGE OF NATURAL GRAPHITE

Yasuo UCHIYAMA, Shin-ichiro MATSUSE and Hideaki SANŌ

*Department of Materials Science and Engineering, Faculty of Engineering,
Nagasaki University,*

1-14 Bunkyo-machi, Nagasaki 852-8521, JAPAN

Introduction

The carbonaceous materials are used not only as structural materials but also as functional materials such as electrode for lithium ion battery. It is known that changing in their texture or structure can control characteristics of carbonaceous materials. Hetero atom loading, especially boron loading promotes textural and structural change of carbonaceous materials [1-2]. We found that lanthanum/boron concurrent loading increased interlayer spacing of petroleum coke and natural graphite (NG) [3-4].

In this paper, we report that the effect of additive ratio of La/B and heat treatment on the structural change of natural graphite. In particular, the structural change behavior of NG with concurrent or successive addition of La/B was examined.

Experimental

NG was used as a carbonaceous material. La_2O_3 and elemental boron were used as an additive. The NG was mixed with La_2O_3 and B separately or concurrently by a mortar for 0.5h. Additive ratio of elemental La and B was varied from 0.25 to 1.00 at.%-La and from 1.50 to 6.00 at.%-B. The mixed powders with 16 levels of additive ratio were heat-treated at the temperatures ranging from 1500°C to 2500°C for 1.0h under argon atmosphere. In successive addition, La_2O_3 was mixed with the NG first and heat-treated at 1500 or 2300°C. After this, residual La that could not load into the NG was solved out by hydrochloric acid, and then boron was mixed and heat-treated again at 1500 or 2300°C. XRD analysis was conducted at R.T. and elevated temperatures for identification of constituent and quantification of graphite crystallinity. Interlayer spacing, c_0 and a_0 were calculated from positions of 002, 004 and 110 peaks of graphite and 111, 311 and 331 peaks of silicon which is added as an internal standard. The concentration of La in the samples after heat treatment was determined by ion micro analyzer (IMA).

Results and Discussion

Figure 1 shows the c_0 value of the NG with La and B separate or concurrent loaded by heat-treated at 2500°C. The samples with concurrent loading of B and La show a significant increase in the c_0 value than the other samples with separately La or B loading and the NG. The increase of the c_0 value for the samples occurred at the temperatures ranging from 1800°C to 2500°C. Interlayer spacing of the samples with additive of La:B = 1:3 at.% was expanded most. c(002) and c(004) peak profiles the samples seem possible to have several peaks and c(006) peak was undetected. The La is little influence on c_0 value at any HTT studied. It was known that La acts as a catalyst for graphitization of petroleum coke [3], though La may have no influence on structural change of carbonaceous material with perfect crystal.

The La concentration of the samples with La separate loading is showed in Table 1. The results point up the difference of La concentration in among the samples. This result strongly suggested that the La existed in the sample without changing of the graphite perfect crystal. To verify the above suggestion, the sample that may contain the La was re-heat treated with B at 2300°C. The peak profile and c_0 value of the successively La/B loaded samples show almost the same as the concurrently loaded sample. This result indicates that La influenced the structural change of graphite cooperatively with boron despite of no change of interlayer spacing in the case of separate loading.

Figure 2 shows the change of c(004) profiles and c_0 value measured by XRD at elevated temperatures. With an increase of temperature, c_0 of the NG increased at regular intervals. On the contrary, c_0 value of the sample named 1L3B23 (1.0at.%-La/3.0at%.-B concurrent loading, at 2300°C) showed the maximum value at 900°C, and gradually decreased to that of the NG above 1000°C. Furthermore, the 1L3B23 sample heat-treated again at the temperatures ranging from 1400°C to 2300°C was examined by XRD at R.T.(Fig.3). The c_0 value of the sample showed the minimum value at 1800°C and

increased again with the increasing temperature. It is conjectured that La and B were intruded in the graphite structure by heat treatment above about 1800°C and caused increasing interlayer spacing. This increasing interlayer spacing was quenched by cooling treatment. During heat treatment up to 1800°C, lanthanum and boron released from the sample, which reverted to a stable structure again at relative lower temperature than that of loading treatment.

Conclusion

Concurrent loading of lanthanum and boron into the natural graphite increased in interlayer spacing.

Lanthanum can intrude into the graphite structure despite of no change in interlayer spacing.

Structural change of natural graphite with lanthanum and boron was reversible change at elevated temperature.

References

1. Hagio T, Miyazaki K and Kobayashi K. Effect of addition of borides on hot-pressing of coke. *Yogyo-Kyokai-Shi* 1979;87(8): 416-422.
2. Hagio T, Miyazaki K and Kobayashi K. Hot-pressing of carbon powder added with LaB₆. *Yogyo-Kyokai-Shi* 1981;89(8): 411-418.
3. Uchiyama Y, Araki S, Sano H and Kobayashi K. Abrupt change with HTT in lattice parameter of petroleum coke and natural graphite mixed with LaB₆. *Carbon* 1994;32(7):1388-1389.
4. Uchiyama Y, Araki S, Sano H and Kobayashi K. Effect of lanthanum compound addition on the lattice parameter of petroleum coke. *Carbon* 1995;33(3): 333-335.

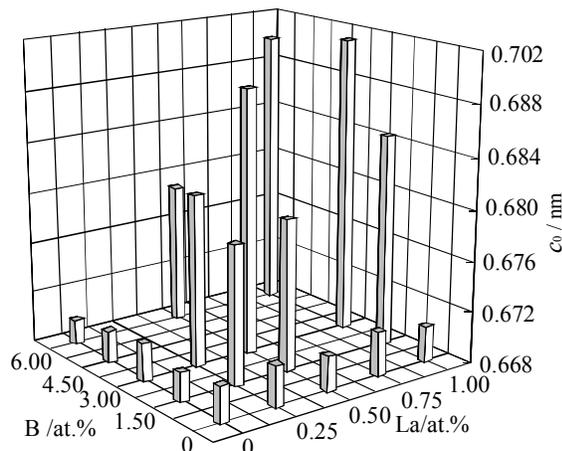


Fig.1 Effect of lanthanum / boron separate or concurrent loading on c_0 value of the natural graphite heat-treated at 2500°C.

Table 1 Lanthanum concentration of the sample with 1at.%-La separate loading at 1500° and 2300°C.

sample	heat treatment temp. / °C	residual La removal	La content / at.%
Sample A	1500°C	no	0.98
Sample B	1500°C	yes	0.05
Sample C	2300°C	no	0.58
Sample D	2300°C	yes	0.38
Sample E*	2300°C	-	0.36

* The sample D re-heat-treated at 2300°C

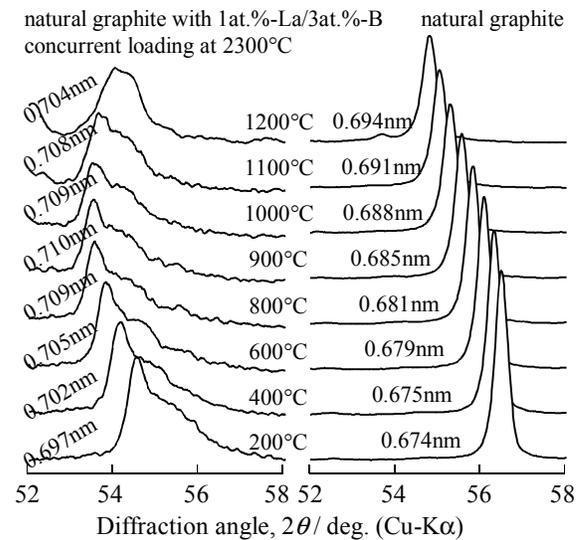


Fig.2 The change of $c(004)$ profiles and c_0 value of the samples measured by XRD at elevated temperatures.

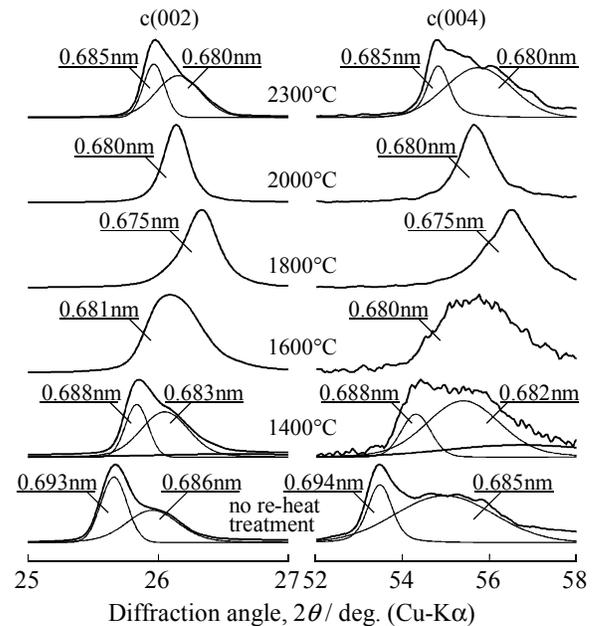


Fig.3 XRD profiles and c_0 value of the samples (1at.%-La/3at.%-B concurrent loading at 2300°C) with re-heat treatment temperature. (measured at R.T.)