EFFECT OF B_2O_3 ADDITION ON SINTERING AND GRAPHITIZATION OF CARBON MATERIALS

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Introduction

Most graphite products are generally fabricated with the use of pitch binder phase, as pitch binder phase is necessary to cement carbon particles for compaction of carbon materials.

K.Kobayashi et al[1] have reported that dense and strong polycrystalline graphite was made by hot-pressing method from calcined pitch coke powder with B_2O_3 addition.

It has been already well known by many investigators[2-6] that boron dissolves substitutionally in graphite structure with a maximum solubility of 2.35% at 2350°C[2]. In the solid solution, the in plane lattice parameter a-spacing increases and d(002) spacing decreases with boron content. There is also evidence that boron in excess of the solubility limit may occupy an interlayer position increasing d(002) spacing.

We have found in addition to these facts that boron derived from boron oxide is effective to sinter coke particles under hot-pressing. This paper describes on some properties of the products made from various kind of carbon materials with B_2O_3 addition and necessary experimental condition for obtaining dense and strong polycrystalline graphite. And the effect of B_2O_3 addition on both sintering and graphitization was also investigated.

Experimental

Pitch coke, petroleum coke, aceton-furfural resing carbon, pyrolytic carbon and carbon fiber were used as starting materials. Except for carbon fiber the raw materials pulverized into fine powders and B_2O_3 added as an aqueous solution. After drying the powder was set in a graphite die of 30mm and heated at various temperature up to 2200°C under a pressure of 200kg/cm^2. In the case of the carbon fiber the fiber dipped in B_2O_3 aqueous solution and after drying it set along one direction in a graphite die, and then hot-pressed under the same condition. After hot-pressing some properties such as, density, mechanical strength, graphitization degree, boron and boron carbide content of the compacts were examined and factors affecting the properties were investigated.

Results and discussion

(1) Effect of Pressure and Temperature

Some pressure during heat-treatment, was known to be necessary for obtaining dense and strong compacts, Without pressure strong compacts could not be obtained. Fig.1 gives behaviour of typical shrinkage couve of the sample with increase of temperature under pressure of 200kg/cm^2. From this curve initial rapid densification occured in the range from room temperature to about 400°C is considered to be due to that B_2O_3 changes to liquid phase and coke particle are rearranged to closer packing within the glass matrix under pressure. Second rapid densification is observed above 2000°C. Hagio et al[7] report in the experiment on hot-pressing of pitch coke with B_2O_3 addition that above 2000°C d(002) decrease, Lc(112) increase and mechanical strength of the compacts increased. Other carbon materials showed same tendency with temperature. From these facts rapid densification above 2000°C is also known to be caused by sintering and graphitization of carbon particles under a pressure with diffusion of boron into graphite structure. In this experiment upper limit of pressure was set at 200kg/cm^2 because of considering safety limit of graphite die and punch. However, it is thought if higher pressure is applied, hot-pressing temperature could be lowered for obtaining same properties of the compacts, or the properties could be improved even at same temperature.

(2) Effect of Content of B_2O_3 Addition

Most suitable content of B_2O_3 addition was a little different on sample to sample. For graphitizing-type carbon such as pitch coke, petroleum coke and pyrolytic carbon 8-12wt% addition was generally found to be most effective for sintering and graphitization to obtain dense and strong polycrystalline graphite. Table 1 gives some examples of the hot-pressed compact at 2200°C made from the powder with 10wt% B_2O_3 addition and with no addition. And Fig.2(a) gives typical example on change of some properties of graphitizing-type carbon such as pitch coke with increase addition of B_2O_3 at 2200°C.

For non-graphitizing-type carbon such as aceton-furfural resin carbon or carbon fiber, suitalbe content of B_2O_3 addition showed some difference on sample to sample. Fig.2(b) gives change of some properties of aceton-furfural resin carbon with increase addition of B_2O_3. In the case of carbon fiber the denser and stronger compacts was obtained at the higher content of B_2O_3 addition. This difference is considered to be due to some difference in shape, texture and structure between raw materials. All these non-graphitizing-type carbon with B_2O_3 addition showed composit (002) reflection profile like similar pattern obserbed on non-graphitizing-type carbon at usual heat-treatment.

3) Some Properties of the Hot-pressed Products at Suitable Experimental Condition.

In addition to these factors above described, powder size distribution and calcining temperature of raw material, method of B_2O_3 addition give some influence of the properties of the hot-pressed compacts. Table 2 gives some properties of hot-pressed products made from various carbon materials with B_2O_3 addition under the suitable condition.

Ref. 1) K.Kobayashi et al, Abstracts 12th Conf. on Carbon, 247 (1975); 2) C.E.Lowell, J. Amer. Soc., 50, 142 (1967) ; 3) J.A. Turnbull et al, Carbon, 3, 387 (1966) ; 4) S.Marinkovic et al, Carbon, 7, 185 (1969) 5) H.Gasparoux et al, Carbon, 3, 65 (1965); 6) W.V.Kotlensky, Carbon, 5, 409 (1967); 7) Sagio et al, in this abstract, 13 Carbon Conf. (1977)

B_2O_3	addition(10wt%)			no addition		
	ρ (g/cc)	S (kg/cm²)	Co (Å)	ρ (g/cc)	S (kg/cm²)	Co (Å)
Pitch coke	2.01	600	6.722	1.77	50	6.823
Petroleum coke	2.03	250*	6.720	1.75	60	6.818
Pyrolytic carbon	2.07	432	6.712	1.57	43	6.839

* Bending

Table 1. Some properties of hot-pressed products from the powder with 10wt% B_2O_3 addition and no addition at 2200°C.

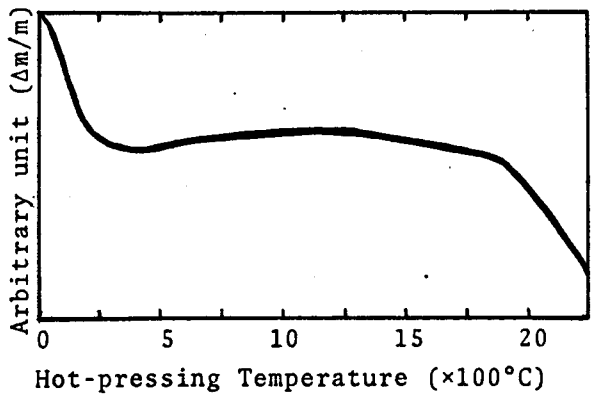

Fig.1 Typical shrinkage curve during hot-pressing

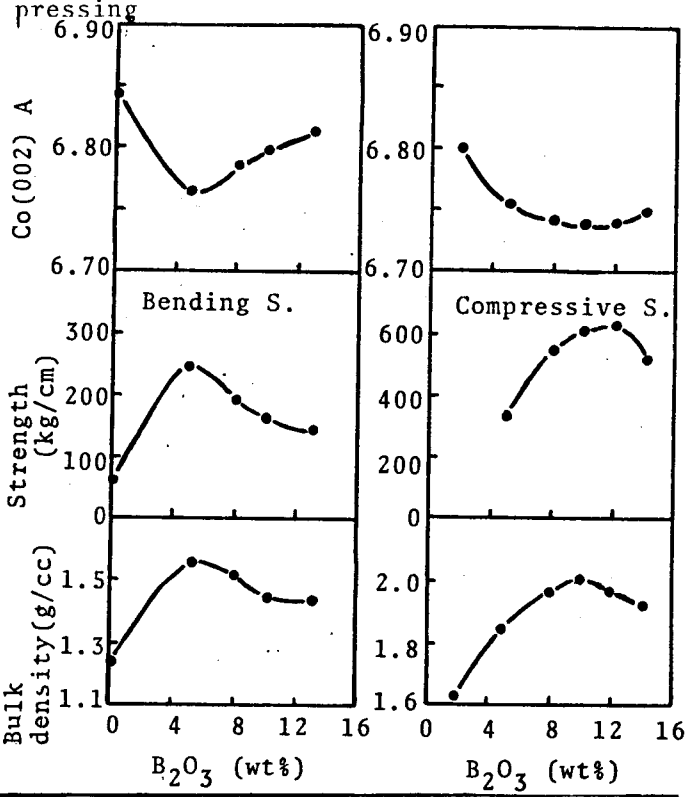

Fig.2. Some prerties of hot-pressed products (a) pitch coke and (b) aceton furfural resin carbon with content of B_2O_3 addition at 2200°C.

	Pitch coke	Petroleum coke	Aceton-furfural resin carbon	Carbon fiber	Pyrolytic carbon	Conventional artificial graphite
Bulk density(g/cc)	2.0-2.1	2.0-2.1	1.6-1.7	1.8-1.9	2.0-2.15	1.6-1.8
d(002) (Å)	3.36-3.37	3.355-3.365	3.37-3.38	3.37-3.38	3.355-3.360	3.36-3.37
Lc(002) (Å)	>600	>1000	300-400	400-500	≥1000	>500
Compressive strength (kg/cm²)	1000	800	1000-1200	—	600-700	500-600
Bending strength (kg/cm²)	600	400	600-700	2000	300-400	200-300
Electric resistivity (μΩcm)	700-1000	500-1000	1	—	—	1000

Table 2. Some properties of hot-pressed products under suitable condition.