EFFECT OF BORON CARBIDE ADDITION ON SOME PROPERTIES OF HOT-PRESSED POLYCRYSTALLINE GRAPHITE MADE FROM COKE POWDER

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Introduction

Recently K. Kobayashi et al[1)] have reported that graphitized high density carbon could be fabricated from coke powder by hot-press method without the use of a pitch binder phase only with the addition of a small amount of boron oxide as a accelerating agent for sintering and graphitization of carbon particles.

From this results it was thought that boron carbide addition might also influence on sintering and graphitization of carbon particles as well as boron oxide. The purpose of this experiment is to clarify some properties of the sintered bodies made from coke powder with boron carbide addition (0-50wt%) and to know the effect of boron carbide on both sintering and graphitization.

Experimental

Calcined pitch coke powder under 149 micron size and boron carbide powder of 1-2 micron size were pulverized and mixed by tungsten carbide motar with different boron carbide addition from 0 to 50wt%. Then each of the mixed powder of 20g with different mixing ratio was set between graphite die and punch, and heated at various temperature from 1400°C to 2200°C and held at the temperature for 60 min under a pressure of 200kg/cm^2 by hot-press apparatus. Rate of heating was 40 min from room temperature to 1800°C, 60 min to 2000°C and 80 min to 2200°C. The compacts obtained after hot-pressing were examined to clarify the effect of boron carbide addition and that of hot-pressing temperature on some properties such as texture, density, mechanical strength, electric resistivity and graphitization degree of coke.

Results and discussion

Disk-shaped compacts of 30mm in diameter and about 12-21mm in height were obtained after hot-pressing of the mixed powder of coke and boron carbide.

Some properties of the compacts were remarkable different with the amount of previous addition of boron carbide and the hot-pressing temperature.

Fig.1 gives the relative density of the compacts after hot-pressing at the temperature of 1800, 2000 and 2200°C with different boron carbide content in originals.

The relative density generally increase with increase of boron carbide content and hot-pressing temperature. The rate of increase is particularly remarkable within 10% addition and maximum density of 96% was obtained in the case that hot-pressing temperature was 2200°C and the boron carbide content was more than 30%.

Fig.2 gives change of the bending strength of the compacts after hot-pressing with increase of boron carbide content in originals. The strength increase with increase of boron carbide content and hot-pressing temperature. The behaviour of increase is particularly outstanding at 2200°C, that is, the value shows a rapid rate of increase in the range less than 30% and reaches to about 1500kg/cm^2 at about 30% addition, then the rate becomes slow with increase of boron carbide content. In either case from the samples with no boron carbide addition or at the hot-pressing temperature below 1800°C, strong compacts could not be obtained. It is known from these data that hot-pressing temperature of at least 2000°C is necessary in order to obtain a dense and strong compact.

Fig.3 gives change of the electric resistivity of the compacts after hot-pressing with increase of boron carbide content in originals. The electric resistivity once decreases with increase of amount of boron carbide addition, and shows minimum value at 10-20wt% addition. The minimum value decrease with increase of hot-pressing temperature. In the case of 2200°C minimum value of $0.9\times10^{-3}\Omega$-cm was obtained at 10wt% addition.

The resistivity has a tendency to increase again in the range above 20wt% addition. This tendency is more outstanding in the case of 1800°C treatment, while the increase rate is very slow or almost constant in that of 2200°C.

Fig.4 gives change of d(002) spacing of coke of the compacts with increase of boron carbide content in originals after hot-pressing at different temperature.

It is known from this result that the effect of boron carbide addition is particularly remarkable at 2000 and 2200°C than at 1800°C. At 1800°C, d(002) decrease continuously with increase of boron carbide addition, but the change is very small. At 2000°C, d(002) decreases rapidly from 3.420 Å at 0% to 3.370Å at 10wt% addition and then it keeps almost constant at about 3.370Å in spite of the increase of the amount of boron carbide. At 2200°C, d(002) decrease more remarkably from 3.388Å at 0% to the minimum value of 3.360Å at 5wt% and then it increases again gradually to about 3.370 Å at 50wt% addition.

In the case of 2200°C apparent crystallite size, La(110) increased rapidly from 400Å at 0% to maximum value of 1200Å at 5wt% addition. At 2000°C, La showed also

maximum value of about 700Å at 5-20wt% addition, while at 1800°C change of La value is not so remarkable with increase of boron carbide addition.

Development of (112) reflection peak was also accelerated at 2000 and 2200°C by boron carbide addition. Lc(112) showed maximum value of about 30Å at 5wt% addition in the samples treated at 2200°C.

It is clear from these X-ray data that boron carbide addition has an effect to accelerate graphitization of coke. Particularly it was most effective in the range near 5wt% addition at 2200°C.

It has already well known by many investigators[2-7] that boron solid-soluted into graphite structure above about 2000°C and give some influence its X-ray parameter. In this experiment boron atom comes from boron carbide also considered to be solid-soluted into coke structure and promote the formation of graphitic structure. Furthermore under the condition of hot-pressing coke particles began to sinter each other with diffusion of boron atom into substitutinal or interlayer position, and the compacts was densified and strengthened above the temperature of 2000°C. From chemical analysis and X-ray analysis solid-soluted boron content was assumed about 1%. In the samples with higher borom carbide content, supply of boron atom into coke particle is thought to be more uniformaly to promote sintering and further linkage between boron carbide and carbon grain might give some effect to raise the compact strength.

References (1) K.Kobayashi et al, Abstract for the 12th Carbon Conf. (1975); (2) F. Tombrel, Rev. Hautes Temper. et Réfract, t, 3, 79 (1966); (3) J.A.Turnbull et al, Carbon, 3, 387 (1966); (4) W.V.Kotlensky, Carbon, 5, 709 (1967); (5) C.E.Lowell, J. Amer. Ceram. Soc., 50, No.3, 142 (1967); (6) S.Marinković et al, Carbon, 7, 185 (1969); (7) Jean-Pierre Rouchy et Jucques Méring, C. R. Acad. Sc. Paris, 277, série C, 533 (1973)

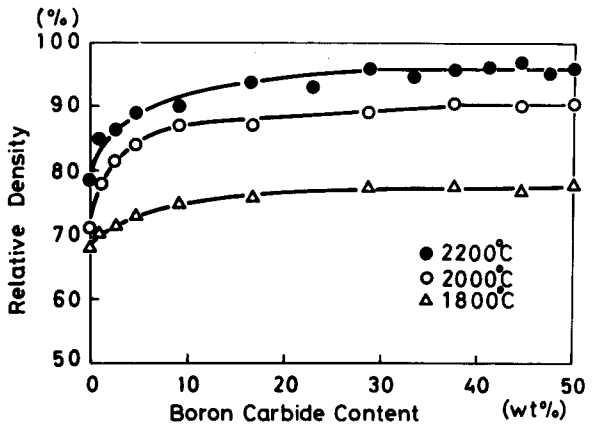

Fig.1 Change of relative density of the compacts after hot-pressing with boron carbide content in originals.

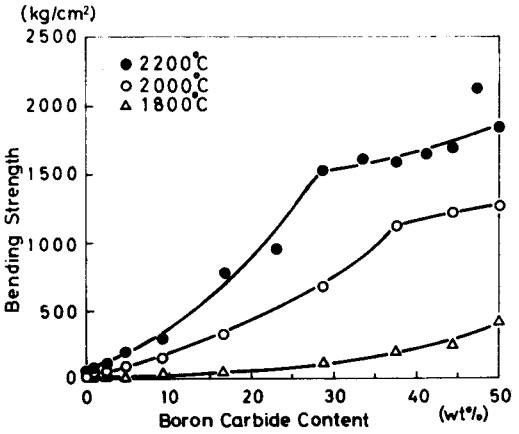

Fig.2 Change of bending strength of the compacts after hot-pressing with boron carbide content in originals.

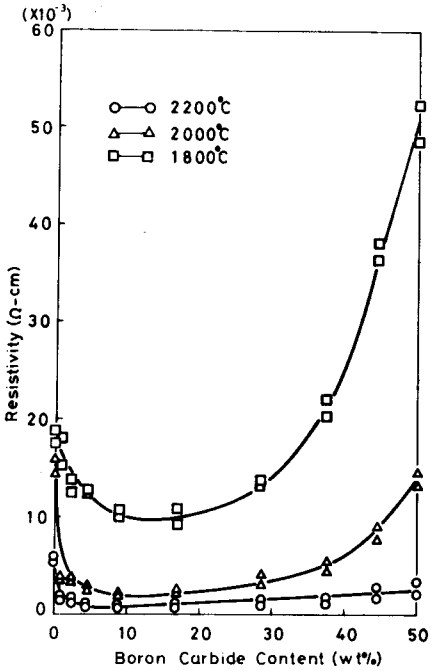

Fig.3 Change of electric resistivity the compacts after hot-pressing with boron carbide content in originals.

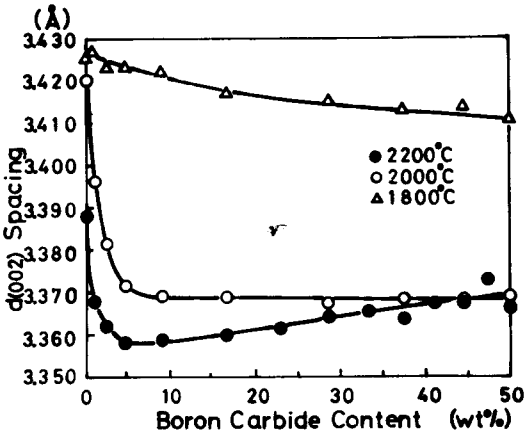

Fig.4 Change of d(002) spacing of coke after hot-pressing with boron carbide content in originals.