Preparation and Characterization of Ultra Fine B-C-N-O Powders by Using a dc Arc Plasma

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Ultra fine B-C-N-O powders were prepared from h-BN, C, and B_2O_3 by quenching chemical species excited in a dc arc plasma on a metal disk cooled with water. The sintered bodies composed of h-BN, C, and B_2O_3 were heated in the plasma flame and were evaporated and ionized, and finally were condensed to the metal disk cooled with water as ultra fine powders. The SEM and TEM micrographs of the powders obtained showed that they agglomerated and consisted of small particles with various shape such as spherical, plate-like, and angular. The X-ray diffraction and the EDAX analysis of them indicated unknown peaks which suggested strong possibility of the formation of a new phase containing B, C, N, and O. The formation mechanism of the powders was briefly discussed from the viewpoint of supersaturation ratio based on classical theory of homogeneous nucleation.

1 Introduction

Since the possibility of diamond synthesis at lower pressure than 1 atm has been indicated by various methods[1-9], much attention has been paid to synthesize a new material with metastable phase by various methods[10]. In the phase diagram of B-C-N-O systems, various metastable phases are well known.. In this connection, recently, a research group at NIRIM successfully developed to produce a metastable phase of a cubic B-C-N compound in high-pressure high-temperature synthesis[11]. However, no papers to suggest the possibility in the preparation of a new materials with metastable phase in B-C-N-O systems at lower pressure than 1 atm have been reported. In this paper, we describe a trial to produce a metastable phase in B-C-N-O systems by using a dc arc plasma.

2 Experimental

A dc arc plasma can produce a very high temperature in which we can introduce reactant materials for preparing chemical species with very high energies. The maximum temperature of it is on the order of 15000K and the velocity of its flame is as high as 300 m/sec. So, if the tail flame of the plasma was quenched on a metal disk cooled with water, it is very convenient to quench chemical species with high energies and to produce metastable phase as well as ultra fine powders.

Resultantly by this process there is a possibility for ultra fine powders with metastable phase to be formed.
The experimental procedure was in the following. The reaction chamber was maintained at 100 torr. The dc arc plasma was operated under the condition of 25V and 450A by using Ar gas. Two kinds of samples for experiment were prepared, a sample A was mixed in the ratio of hBN : B_2O_3 : C=1 : 6 : 3 in weight, a sample B was in hBN : B_2O_3 : C=1 : 1 : 1. The samples were mixed for 30 min in an agate mortar. The resultant samples were pressed in the shape of cylinders about 20mm long and 5mm in diameter at 10 MPa. The cylinders pressed were sintered for 2 h at 800°C in air. The sintered samples of A and B were used for the preparation of ultra fine powders in B-C-N-O systems, but in this paper, the data of the sample A were mainly discussed.

Fig. 1 showed a schematic illustration to prepare ultra fine powders in B-C-N-O systems. The sintered samples set on a quenching disk cooled with water were heated in the plasma flame and were evaporated, decomposed, and ionized to chemical species with high energies as shown in the figure. The plasma flame was rapidly cooled on the quenching disk and the chemical species in the plasma were nucleated on the quenching disk cooled with water as ultra fine powders. The resultant powders deposited on them were collected. The powders collected were characterized by X-ray diffraction, scanning electron microscopy(SEM), transmission electron microscopy(TEM), and others.

3 Results and discussion

Fig. 2 showed a SEM micrograph of the powders collected on the quenching disk. As can be seen in the figure, the powders agglomerated and consisted of small particles with various shapes such as angular, sheet-like, and spherical ones. As mentioned later, X-ray diffraction pattern showed that unreactive B_2O_3 and hBN existed in the agglomerated particles. The unreactive B_2O_3 would particularly play an important role in the formation of the agglomerated powders. Since the melting point of B_2O_3 is low about 577°C, it would act as a binder to form the agglomerated particles, since the liquid phase of the B_2O_3 would be an adhesive because of its high viscosity. Some grains in the particles had sharp crystal habits. As an example, Fig. 3 showed a grain with sharp crystal habits. According to the EDAX analysis of the grain, B, C, N, and O were clearly detected as shown in Fig. 4. This would suggest the formation of a new phase with B, C, N, and O, since a compound containing B, C, N, and O has not yet been reported. Fig. 5 showed an X-ray diffraction pattern of the powders collected on the quenching disk. We can see the diffraction peaks of B_4C formed by a reaction between B_2O_3 and C or hBN and C, and those of unreactive hBN and B_2O_3. However, interestingly from the figure, the X-ray diffraction pattern clearly indicated unknown diffraction peaks as shown by arrows. This may also suggest a strong evidence of a new phase formed.

According to the classical theory of homogeneous nucleation., the nucleation radius from supersaturated vapor is mainly proportional to $\log_e P/Po$, supersaturation ratio, where P is actual vapor pressure and Po is equilibrium vapor pressure. In the case of our present experimental data, the plasma temperature decreases very rapidly on the quenching disk cooled with water. As a result, the equilibrium vapor pressure rapidly decrease with the temperature. The nucleation rate of powders from chemical species in the plasma is estimated to be very fast and the nucleation would be carried out instantaneously. The increasing supersaturation ratio with decreasing plasma temperature is expected to enhance the nucleation of the powders. The velocity of a dc arc plasma is about 300m/sec. At the velocity, the time to pass through 1 cm in the vicinity of the quenching disk and wall is about $7X10^{-5}$sec, the growth rate of the powders is estimated on the order of $7X10^{-2}$ nm/sec. Within such a short time, it is difficult to for the average size of powders to reach 100nm. Therefore, it is speculated that the powders nucleated from chemical species on the quenching disk would be agglomerated by the Brownian movement to form a particle during their transportation in the stream of the plasma from the disk to the wall.

As indicated in the X-ray diffraction pattern, unreactive hBN and B_2O_3 clearly existed in the powders. This indicates in such a reaction system that the reaction among B_2O_3, C, and hBN does not perfectly take place. As the reasons for this, it is considered that, firstly as mentioned, the reaction time is very short because of the very fast velocity of the flow in the dc arc plasma jet, and secondly the reactant materials do not ionize because of high specific heat capacity. In order to evaporate and ionize perfectly the reactant materials, we tried to inject very fine powders into the plasma through a powder feeder with a carrier gas of Ar. However, in this case, no good results did not obtained. Further work will be carried out about this.

In summary, ultra fine B-C-N-O powders were prepared from h-BN, C, and B_2O_3 by quenching chemical species excited in a dc arc plasma on a metal disk cooled with water. The SEM and TEM micrographs of the powders obtained showed that they agglomerated and consisted of small particles with various shape such as spherical, plate-like, and angular. The X-ray diffraction and the EDAX analysis of them indicated unknown peaks which suggested the formation of a new phase containing B, C, N, and O. The formation mechanism of the powders was briefly discussed from the viewpoint of supersaturation ratio based on classical theory of homogeneous nucleation.

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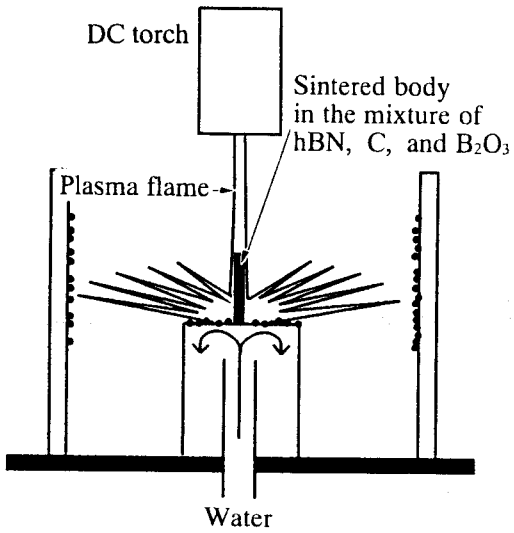

Fig. 1 A schematic illustration to prepare ultra fine powders in B-C-N-O systems.

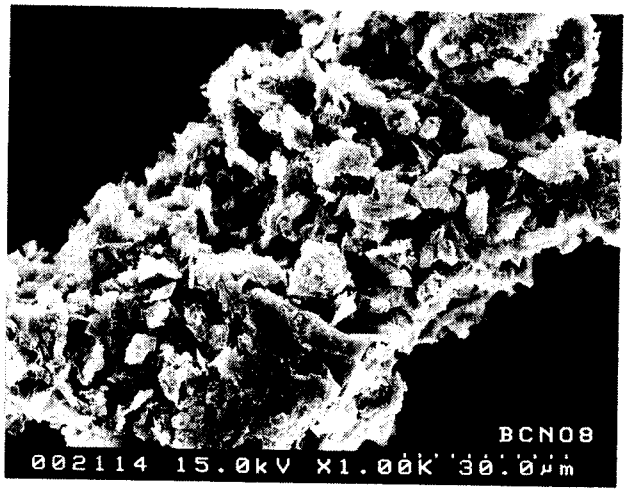

Fig. 2 A SEM micrograph collected on the quenching disk.

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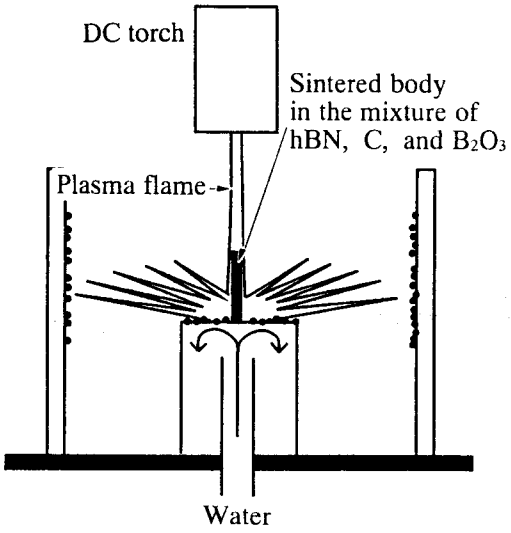

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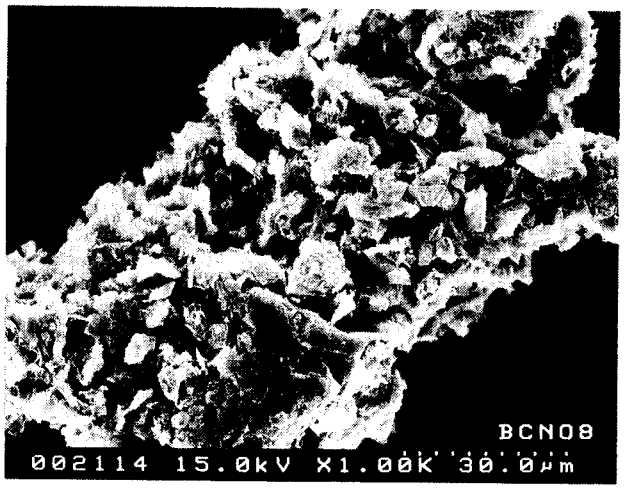

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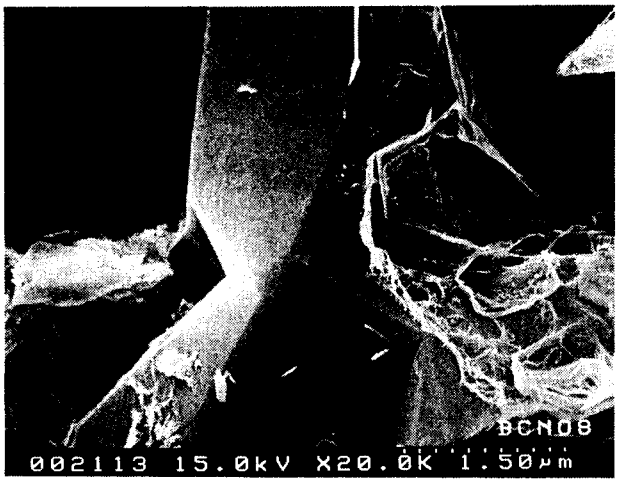

Fig. 3 A SEM micrograph of a grain with sharp crystal habits.

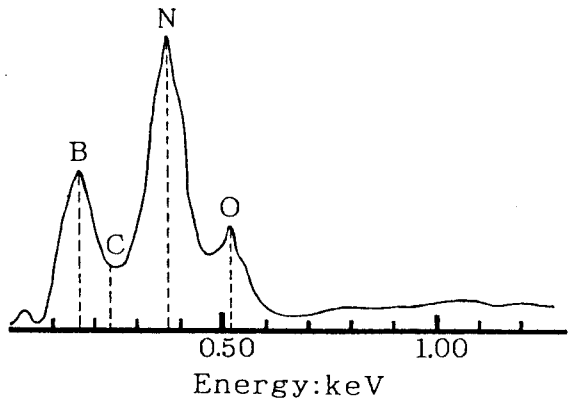

Fig. 4 The EDX analysis of the grain in figure 3. B, C, N, and O were clearly detected

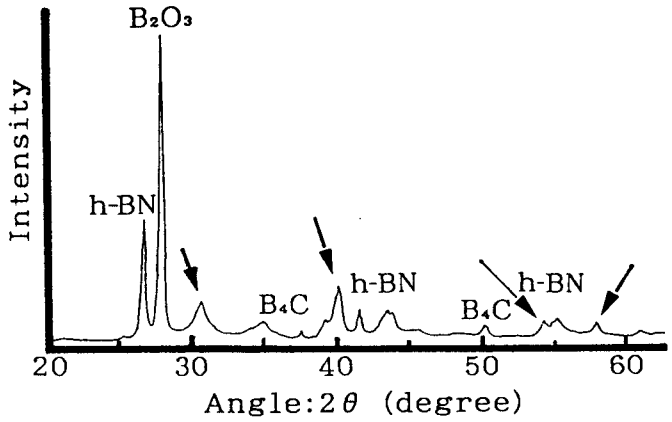

Fig. 5 An X-ray diffraction pattern of the powders collected on the quenching disk.