Evaluation by extended Hückel method on the hardness of the B–C–N materials

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Abstract

Hard materials, e.g. diamond and cubic boron nitride (c-BN), are widely applied to improve the lifetime and the performance of many kinds of cutting and forming tools. These materials are usually used at high temperature, so the study of stability on these materials at high temperature is very important. However, diamond is a low resistance to the oxidation, it should be replaced with the boron-based hard materials. Recently, boron–carbon–nitrogen (B–C–N) ternary materials are expected to possess a high hardness, a high thermal stability at high temperature. We estimated the hardness and the stability of B–C–N materials at high temperature by the extended Hückel method. The extended Hückel method is one of the molecular orbital calculations and needs the cluster model of materials for the calculation. The cluster model of B–C–N materials was regarded as a zinc blende structure. In the present work, we used two physical quantities, i.e. a cohesive energy and an energy fluctuation, as a measure of hardness and stability of materials. The cohesive energy indicates the coherence of bonds between atoms. The energy fluctuation shows the reactivity of materials. Hardness, structure, solid-state properties and reactivity of materials can be estimated from these physical quantities. When the composition of B–C–N materials was boron: 25 at.%, nitrogen: 25 at.% and carbon: 50 at.%, the cohesive energy was the lowest. This result implies B–C–N ternary materials are not harder than c-BN and/or diamond. Cubic-BN was the lowest energy fluctuation of B–C–N materials, and the energy fluctuation increased as increasing of carbon atom. The reactivity of B–C–N materials was high at a high temperature with an increase of carbon atoms. These results imply that B–C–N materials are not suitable for the hard cutting materials.

Keywords: B–C–N; Hard materials; Diamond; c-BN; Extended Hückel method

1. Introduction

Hard materials have been used to improve the lifetime and the performance of many kinds of cutting and forming tools. Especially, hard materials have been expected to be sophisticated in respect of the frictional wear for the purpose of high-speed cutting. For mechanical applications, although diamond is known as the hardest substance, oxidation at high temperatures and poor abrasive resistance for iron-based alloys restrict industrial use. Diamond is started oxidation from 873 K in air, so diamond-cutting tools should be used only at low temperature [1,2]. It is neither stable in the presence of oxygen even at cutting moderate temperatures, nor is it a suitable abrasive for machining ferrous alloys. While c-BN is the next hardest after diamond, it is more chemically stable than diamond. B–C–N ternary materials with a diamond-like structure in which some of the carbon atoms are replaced with nitrogen and boron are expected to show the same interesting properties found in diamond and c-BN, such as hardness, wide band gap, high melting points and the high oxidation resistance. Many researchers have been tried to synthesize B–C–N ternary materials with diamond like structures [3–13]. But B–C–N ternary materials are synthesized hardly. The cubic B–C–N materials are a very liable to the phase separation, because they are was scratching fragile bonds, such as C–N bonds, by high-energy ion irradiation during B–C–N materials deposition and remained c-BN or amorphous carbon [7]. Moreover, the interpretation of a more and more graphite-like structure in case of increasing the nitrogen content is supported by the \( \pi-\pi^* \) transition in the EELS spectra [8]. This result was related another report, which the young’s modulus and the hardness of B–C–N films decreased with increasing the nitrogen contents [9]. While Tateyama et al. calculated about BC\(_2\)N materials and found that \( \beta\)-BC\(_2\)N is the most stable among the possible heterodiamond structures obtained from graphitic BC\(_2\)N without atomic diffusion [10]. They estimated that the zero
pressure bulk modulus of $\beta$-BC$_2$N is found to be 438 GPa. Mattesini et al. studied the stability and the hardness of two novel orthorhombic BC$_2$N structures obtained from a full geometry relaxation of the substituted fcc diamond [11]. Considering the correlation between the hardness and the shear modulus and the values of the bulk moduli, they predict that the two phases of BC$_2$N could be harder than c-BN. A cubic BC$_2$N phase has been synthesized in the ternary B–C–N materials under well controlled pressure-temperature conditions using a laser heated diamond-anvil cell and a multi-anvil press by Solozhenko and co-workers [12]. They reported that the hardness of c-BC$_2$N is higher than that of c-BN single crystals, which indicates that the synthesized phase is only slightly less hard than diamond.

In this paper, we calculated cubic B–C–N materials by the extended Hückel method, and estimated the hardness and stability of cubic B–C–N materials at high temperature.

2. Method of calculation

2.1. Cohesive energy and energy fluctuation

In the present work, we used two physical quantities, i.e. cohesive energy and energy fluctuation, as a measure of stability of substances. The cohesive energy indicates the coherence of bonds between atoms. The energy fluctuation indicates the reactivity of materials. These quantities can be calculated by the extended Hückel method. The extended Hückel method is one of molecular orbital calculations [14,15] and this method needs orbital exponents [16,17] and ionization potentials [18] of each atom as parameters. Then, if the position coordinates of each atom of a cluster is given as input data, the total energy, quantized energy levels, molecular orbitals and Mulliken’s populations [19] are calculated. Using these quantities, cohesive energy and energy fluctuation are estimated follows:

Cohesive energy

$$\text{Cohesive energy} = (\text{total energy of a materials}) - (\text{sum of energy of isolated atoms})$$

$$= E - \sum P Ep$$

Note that

$$Ep = \sum r nIr$$

Where the energy of an isolated atom is given by the sum of the ionization potentials, $Ir$ is the ionization energy of No. $r$ orbital and $n$ is electron numbers.

Energy fluctuation $\Delta E$ is evaluated as a standard deviation of total unoccupied orbital energy based on highest occupied molecular orbital (HOMO),

$$\Delta E^2 = \langle (E_n - \langle E_n \rangle)^2 (E_n) \rangle = \frac{\sum_{n=1}^{k} E_n \exp(-E_n/kT)}{\sum_{n=1}^{k} \exp(-E_n/kT)}$$

2.2. Cluster models

Calculated values of cohesive energy and energy fluctuation depend on the size and surface of the clusters. To discuss the actual stabilities of materials based upon these values, the cluster size dependence of the values and the effects of the cluster surface on the values must be eliminated. A spherical shape has been chosen to eliminate the effect of the surface. The number of atoms contained in a spherical cluster has been changed in order to see the cluster size dependence. When the changes in cohesive energy and energy fluctuation with the change of chemical compositions are calculated, fixed numbers of atoms in a cluster in diamond structure, i.e. 101 atoms in a zinc blend structure, have been used, and respectively solvent atoms are replaced randomly by boron, carbon or nitrogen atoms. In this work, we assumed that the structure of B–C–N materials is regarded as a zinc blend structure. We adopted the interatomic distance of diamond and c-BN in Table 1 [20].

3. Results of calculation

3.1. The stability and the hardness of diamond and c-BN

The purpose of the present work is to discuss the hardness and the stability of cubic B–C–N materials. Before taking up main question, it is necessary to estimate the hardness and the stability of diamond and c-BN. Fig. 1 shows that the energy fluctuation about diamond and c-BN. The energy fluctuation of diamond and c-BN were increasing until at 400 K. Over 400 K, diamond was increasing the energy fluctuation with increasing temperature.
temperature, but that of c-BN was low even if at high temperature. This results showed c-BN is stable materials at high temperature and implies c-BN is suitable for hard cutting materials. We calculated about the cohesive energy of diamond and c-BN, the results are shown in Table 2. The cohesive energy of diamond was a little larger than that of c-BN. This result was an appropriate, because diamond is harder than c-BN.

3.2. The evaluation of bond type for C–B and C–N binary materials

Before we argue the hardness of B–C–N materials, we should estimate the bond type of B–C–N materials. Because the cohesive energy is able to use a measuring stick of hardness, but do not indicate essential hardness of the materials. We calculated about atomic population and atomic bond population of B–C–N materials. Atomic population and atomic bond population is defined as an electron density and bond order by Mulliken [19]. The bond type of materials can be discriminated by these parameters [21]. Table 3 shows that the atomic population and the atomic bond population cubic B–C–N materials. The locative letters of atomic and bond in Table 3 correlates letters in Fig. 2. Yamamoto defined that when atomic population is plus and large and atomic bond energy is near zero, the bond type is covalent bond [21]. The result was that the bond type of diamond, c-BN, cubic C–B and C–N binary materials was covalent bond. Liu et al. mentioned that the bond of cubic C–N is not so hard, because unbinding orbital would be occupied [22]. But cubic C–N had a covalent bond in our result, which was different from Liu’s view. We do not have any idea about this confliction.

3.3. The calculation of cubic B–N, C–B, C–N binary materials

We calculated about the cohesive energy and the energy fluctuation of cubic B–N binary materials (Figs. 3 and 4). The lattice constant of cluster model was adopted c-BN one in

| Materials | Diamond | c-BN |
|-----------|---------|------|
| Cohesive energy (eV) | 7.4141584 | 7.2184768 |

Table 2
Cohesive energy of diamond and c-BN

Table 3
Atomic population and atomic bond population of diamond, c-BN, cubic C–N and C–B materials

| The locative number of atomic and bond | Atomic population | Atomic Bond Population |
|----------------------------------------|-------------------|------------------------|
|                                       | A                 | B, C                  | D, E | A-C, B-C | C-D, C-E |
| Diamond                               | 2.682521          | 2.699558              | 2.655860 | 0.396118 | 0.399466 |
| c-BN                                  | 5.439963          | 0.798391              | 0.789775 | 0.272270 | 0.273826 |
| Cubic C–N                             | 1.640206          | 4.200884              | 4.219916 | 0.329132 | 0.330192 |
| Cubic C–B                             | 3.431248          | 1.294426              | 1.303454 | 0.363108 | 0.363322 |

Table 1, where 100 at.% boron and nitrogen clusters are hypothetical models. Vertical line means composition of the materials. When boron atomic ratio of binary B–N materials was 47 at.%, the cohesive energy was a maximum energy (Fig. 3). So when the ratio boron and nitrogen is equivalent, c-BN is the hardest of other cubic B-N binary materials. Fig. 4 is the energy fluctuation of binary B–N materials. The energy fluctuation increased with increasing the temperature. When the ratio of nitrogen atom was 47, 50, 54, 60, 80 and 86 at.%, the energy fluctuation was a low relatively. When it was about 50, 60, 80 at.%, c-BN was stable. We calculated about the cohesive energy cubic C–N and C–B binary materials (Fig. 4). The lattice constant of cluster model was adopted diamond one in Table 1. The cohesive energy of C–N and C–B binary materials was decreased with increasing the nitrogen or boron replaced atoms. These binary materials were not harder than

Fig. 2. The unit lattice of zinc blend structure. (A): diamond, (B): c-BN (●: nitrogen, ○: boron), cubic C–B (●: carbon, ○: boron), cubic C–N (●: carbon, ○: nitrogen).

Fig. 3. Change in cohesive energy with the change of chemical composition of cubic B–N binary materials.
diamond. Especially, the decreasing ratio of the cohesive energy for C–N binary materials was larger than C–B binary materials. Boron and nitrogen doping in diamond material was not significant in view of hardness. Another important knowledge was that boron and nitrogen atoms did not form the solid solution with carbon atoms. Because the characteristic of solid solution formation atoms is that the cohesive energy changes linearly (alternate long and short dash line in Fig. 4) with changing their composition. But the trace of the cohesive energy of C–N and C–B binary materials excursed the line. These results affirm Ulrich’s work [3]. Figs. 5 and 6 showed the energy fluctuation of C–N or C–B binary materials. The energy fluctuation of C–N binary materials was very stable, when the composition of nitrogen was 90 at.% (Fig. 5). While, there were no significant result in C-B binary materials (Fig. 6).

3.4. The calculation of cubic B–C–N ternary materials

Cubic B–C–N ternary materials were calculated about the cohesive energy (Fig. 7). The lattice constant of cluster model was adopted c-BN one in Table 1. The cluster model adopted c-BN, and atoms of the cluster replaced carbon atoms randomly. When the composition of B–C–N materials was boron: 25 at.%, nitrogen: 25 at.% and carbon: 50 at.%, the cohesive energy was the lowest. This result implies cubic B–C–N materials material (especially c-BC2N) is not harder than c-BN and/or diamond. E. Knittle et al. synthesized cubic C/(BN)1−x solid solution by the laser-heated diamond cell [13]. They compared the isothermal bulk moduli for diamond, c-BN and C/(BN)1−x. When X = 0.5, the bulk modulus of cubic B–C–N materials is lowest. Their experimental results related with our result, where c-BC2N was not harder than diamond and c-BN. Fig. 8 showed the energy fluctuation of cubic B–C–N materials. The energy fluctuation of c-BN was the lowest, and the energy fluctuation was increasing remarkably with replacing carbon atoms at high temperature. From this result, the reactivity of B–C–N materials was increasing by adding carbon atoms at high temperature, materials which are included carbon atoms is not appropriate for heat-resistant materials Fig. 9.
4. Conclusion

We calculated the cohesive energy and the energy fluctuation of cubic B–C–N ternary materials by the extended Hückel method. The results show that cubic B–C–N ternary materials are not solid solution, and not harder than diamond and/or c-BN, and not stable at high temperature. We found that cubic B–C–N ternary materials are not appropriate for hard cutting tools.

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Fig. 9. Change in fluctuation energy with the change of chemical composition of cubic B–C–N ternary materials.