GRAIN SIZE DISTRIBUTION AND MORPHOLOGIES OF NANOCRYSTALLINE BORON-NITRIDE DURING BALL MILLING

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Abstract — The ball milling process of boron nitride powders has been investigated by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM). During the early stage of milling, the grain size of boron nitride decreases rapidly and reaches a stable value of about 10~15 nm after milling for 4~5 h. It has been found that crystalline boron nitride may be vitrified by extended milling, and that boron nitride grains exhibit a plate-like morphology during the whole milling process. Rosin and Rommlar's equation $y = \exp[-(k/x)\gamma]$ can be successfully applied to describe the grain size distribution of boron nitride during the last stage of milling. Parameters $k$ and $k''$ are extrapolated in terms of the R-R equation and can be used to characterize the variation of grain sizes during the milling process.

1. INTRODUCTION

Recently, the ball milling technique has been widely utilized in producing nanocrystalline materials. Fecht et al. (1) have prepared the nanometer-sized pure metals by this method in a series of b.c.c. and h.c.p. systems with the ultimate grain sizes of 9 nm and 13 nm, respectively. Subsequently, Eckert et al. (2) have found that f.c.c. metals with nanocrystalline structure can also be prepared in this manner, which has been previously claimed to be ineffective energy storage. In addition, many nanometer-sized refractory compounds have been synthesized by high-energy ball milling. Morris et al. (3) have found that borides (CrB, CrB2) may transform into their counterparts of supersaturated solid solution with a crystallite size less than 10 nm after 20 h of milling, and amorphous phases by an extended milling. However, previous studies placed more emphasis on the change of grain size, especially the “average effect,” but neglected the evolution of the morphologies or the size distribution of grains. This may lose some valuable information underlying the milling process.

In this work, we have selected boron nitride (BN) as starting powders to prepare nanocrystalline ceramics by ball milling. The hexagonal structure BN, a useful ceramic with a high melting temperature (~3300 K), is of considerably theoretical interest and technological importance due to its simple lattice structure and unique properties.
Generally speaking, the normal or lognormal function can be used to describe the grain size distribution for polycrystalline materials (4), the grains of which can be considered contiguous. For a noncontiguous system such as a collection of single crystals or second phases in a matrix material, the illustration of the grain sizes may be different. The grains for milled powders are neither completely contiguous nor noncontiguous, but in a blended state. In such a circumstance, an individual particulate may be a single crystal, a bicrystal, or a polycrystal.

In the present study, the grain size distribution is obtained by an IBAS photo-analysis system, it can give the relationship between grain numbers and grain sizes. The basic principle is: for any one of the sections of a grain with an arbitrary shape, one can get a circle of equal area to the one of the section, and the diameter of the circle is considered to be the measured grain size. Obviously, the grain size determined by this method is largely dependent on the position of the section we have selected. Compared with the common grain size distribution, the obtained BN grain size distribution is abnormal. It is also found that such a distribution can be described by the Rosin and Rommlar equation (5). An empirical function was used to describe the particle size distribution for milled powders within a millimeter range.

2. EXPERIMENTAL PROCEDURE

Commercially available BN (≥98 wt pct) powders with particle sizes less than 10 μm were chosen for this experiment. The milling experiment was performed in a planetary ball mill, using wear resistant steel balls and a stainless steel vial with a ball-to-powder weight ratio of 16:1. The powders were sealed in the vial with a rubber O-ring in an argon atmosphere. After different milling times, the process was interrupted and some milled powders were taken out for analysis. In order to assess other characteristics, the milled powders were chemically washed with an HCl ethyl-alcohol solution, since no borides react with common acids.

XRD patterns were taken with a Rigaku (D/max-rA) diffractometer, with Cu Kα radiation. TEM observations equipped with an energy dispersive X-ray (EDX) were carried out in a Philips TEM 420. Additionally, TEM dark-field imaging (DFI) (all with the same magnification) was performed using an IBAS photo-analysis system for the statistics of grain size. An equi-circle method was used to determine the grain sizes. The iron content was determined by the analysis of a CAMEBAX-MICRO-type microprobe. The samples for TEM observation were prepared as follows: first, vibrating the milled powders in an alcohol solution by an ultrasonic device, then depositing the ultrafine fragments on a copper grid covered by a thin carbon film in the solution.

3. RESULTS AND DISCUSSION

XRD patterns for BN powders after various milling times are shown in Figure 1. One can see that the unmilled BN powders are composed of hexagonal structure BN and a small amount of amorphous phase. With increasing milling time, all diffraction lines broaden, indicating a continuous decrease in grain size and the introduction of lattice strain. (The strain should be presumably small for BN due to being a brittle material.) In addition, the disappearance of almost all BN diffraction lines after 25 h of milling indicates that the BN grains have been significantly refined and even an amorphization process may have occurred. It has also been observed that a new diffraction peak appears and increases in intensity with increasing milling
time. This may be attributed to the introduction of iron impurity due to wear debris from milling tools, causing the color of BN powders to change from white to black. However, the iron contents of milled powders can be removed by chemical washing, which can be identified by microprobe results. For the powders after 15 h of milling, iron content can be reduced from 0.3 to 0.03 at.% by washing once.

Figure 2 shows the variation of BN grain sizes vs. milling time. Considering the effect of grain shape, grain size was determined in two reciprocally perpendicular directions by (110) and (004) diffraction planes, respectively. Grain sizes were determined by Stocks method (6). During the early stage of milling (less than 4–5 h of milling), the grain sizes in either [110] or [001] directions decrease dramatically, as shown in Figure 2, and reach a critical value of about 9 nm in the [001] direction. The grain sizes in this direction may decrease continuously. However, the determination of such a change cannot be resolved by XRD analysis. Within the milling period of 5–10 h (the last stage of milling), the grain size in the [110] direction finally gets to a stable value of about 13 nm.
The hexagonal structure of BN is schematically shown in Figure 3, it is analogous to graphite in structure. A large lattice expansion in c-direction ([001] direction) indicates a weakened interlayer bond. The bonding energy between the flat networks was reported to be 16.7 kJ/mol (7), whereas the B-N bonding length, joining each atom in its coplanar ring, is considerably less than the sum of the single-bond covalent radii of boron and nitrogen (0.158 nm). This suggests that the fracture of the flat network is relatively difficult. Therefore, a rapid reduction of BN grain sizes should be attributed to the weak interlayer bonding force and/or the interlayer movements.
During the early stage of milling, the ratio of BN grain size in the [110] direction to that in the [001] direction fluctuates around a value of two (Figure 4); this may be related to the plate-like morphology of BN grains. As demonstrated in Figure 5, fine BN grains with plate-like shape are evident.

The results of treatment for DFIs are shown in Figure 2. One can find that the mean values (arithmetic average) fall in a gap between the grain sizes obtained from x-ray (110) and (004) diffraction lines, suggesting the average sizes of plate-like grains. In addition, the grain size distribution for BN powders after 9 h of milling is also obtained and shown in Figure 6. Assuming that the grain size distribution in the milled powders is continuous, one can find that the distribution is quite similar to an exponent distribution other than a conventionally normal or lognormal one. The grain size distributions obtained are closely related to the method employed. There are a lot of methods available to determine the grain size, including length, area, volume or their combinations. Our measuring method depends on the planar sections of grains.

As early as the 1930s, Rosin and Rommlar had put forward an equation (later known as R-R equation) during the investigation of grinding of coal for powdered fuel. It has been successfully applied to determine the particle size distribution of pulverized fuel as the importance...
of size distribution in the industrial uses of coal (8). The empirical R-R equation has a common form as

\[ y = \exp[-(x/k)^n] \]

in which \( y \) is the weight percentage (8) or probability (9) corresponding to particle size \( x \) (in Figure 6, the grain number was approximately used instead of the probability). \( n \) the distribution factor (ranging from 0.5 to 1.5), and \( k \) the size factor. \( n \) and \( k \) are constants for a given test condition. This equation has proved to be complicated for ordinary use. By a simple mathematical transformation, one can make it convenient for determining the constants of \( n \) and \( k \) by an experimental method. Equation [1] can be rewritten as

\[ \log(\log(y^{-1})) = n \log x + C \]

Obviously, one can get a straight line with a slope of \( n \) and an intercept of \( C \) (\( C = \log(\log e) - n \log k \)) when plotting \( \log(y^{-1}) \) vs. \( x \) on the double-log axes.

Figure 7 shows the adaptation of eq. [2] for BN grain size distributions after 4, 9, and 15 hours of milling, respectively. The R-R equation has been originally used to describe distributions of larger particle sizes (\( \geq 10 \mu m \)) exclusively, and this is first reported that the equation is also valid for grain size distribution, particularly in the nanometer scale. Additionally, the result obtained
The separated grains are very rare after 15 h of milling due to the further refinement of the microstructure. Only about fifty grains are counted in almost the same number of DFIs as that after 4 h or 9 h of milling, and seemingly, the fitting of these results to R-R equation is somewhat far-fetched (Figure 7). In general, the equation is valid only for a limited variable \( x \). Beyond an upper limit, the straight line will deviate, as seen in Figure 7. The values of distribution factor \( n \) and size factor \( k \) for BN powders after different milling times are extrapolated from Figure 7 and listed in Table 1, together with the values of \( k^n \) as a modification for \( k \). From Table 1 one can see that the value of \( n \) after 9 h of milling is larger than that after 4 h of milling. Large values of \( n \) indicate a relatively narrow distribution of grain sizes, and small values of \( n \) indicate more equally distributed grains. There is a larger difference between the value \( k \) and the grain size obtained by XRD analysis for the same milling time range (Table 1). This may support the idea that the size factor \( k \) is only a relative value (8). However, the value of \( k \) after 9 h of milling is slightly larger than that after 4 h of milling. The result implies that the change of grain size vs. milling time obtained by the derivative method appears to be contradicted with that by XRD (see Figure 2), which has shown that the grain size after 9 h of milling is several nanometers less than that after 4 h of milling (i.e., the curve from (110)). In addition, the magnitude of \( k^n \) after 4 h of milling (7.0 nm*) is of the same order as the grain size obtained by (004) x-ray diffraction line (9.1 nm) for the same milling time range, and \( k^n \) (12.8 nm*) approximates the value of grain size (12.2 nm) determined by (110) instead of (004) x-ray line after 9 h of milling.

Gilvary (9) derived an equation from a theoretical basis for fragment distribution in a single fracture. It has a form

\[
y = 1 - \exp\left(-\frac{x}{k}\right)
\]

This relation can be considered as the simplification of R-R equation for the case \( n = 1 \). Gilvary suggested that the R-R equation had been established empirically for the case of comminution by repetitive means (usually by milling) (9). In fact, when multiplied \( l/k^n \) on both sizes of eq. [1], it

<table>
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<th>Milling time (h)</th>
<th>XRD (nm)</th>
<th>TEM (nm)</th>
<th>( k ) (nm)</th>
<th>( n )</th>
<th>( k^n ) (nm*)</th>
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<td>4</td>
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<td>17.0</td>
<td>12.0</td>
<td>6.5</td>
<td>1.04</td>
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<td>- - -</td>
<td>12.2</td>
<td>10.2</td>
<td>7.1</td>
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</tr>
<tr>
<td>15</td>
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<td>- - -</td>
<td>- - -</td>
<td>2.8</td>
<td>0.97</td>
</tr>
</tbody>
</table>

*Indicates the unit of \( k^n \) is not an integer.
Figure 5. TEM showing fine BN grains with plate-like shape.

Figure 6. Grain size distribution for BN powders after 9 h of milling.
can be rewritten as

\[
y/k^n = 1/k^n \exp\left(-1/k^n \right) x^n \tag{4}\]

Assuming \(y/k^n = Y\) and \(x^n = X\), one can obtain

\[
Y = 1/k^n \exp\left(-1/k^n \right) X \tag{5}
\]

where \(k^n\) is a constant, depending largely on milling time. Apparently, variable \(X\) obeys a distribution similar to a form expressed by eq. [3]. In this case, \(X (x^n)\) can be assumed as the modification of \(x\), and \(Y\) the probability which has an intrinsic relationship with the grain size (i.e., the value \(k\)). It is also logical to regard eq. [5] as an expression for a single fracture. According to the consideration mentioned above, the milled product for a specified milling time will be the result of an assumed single fracture, and \(k^n\) can be naturally used as an average size for the fragments of such a single fracture. For BN powders, this kind of “single fracture” will undoubtedly result in a change of grain sizes or redistribution of grains, similar to the case in the formation of the fragments of a brittle material in a single fracture.

Actually, the grain sizes determined by DFIs are the cross-sections of grains. They are obtained by cutting these grains with intersecting planes along some crystalline orientations. The grain sizes obtained by the treatment of DFIs possibly result from several differently crystalline orientations of BN grains, but their indices are not determined correspondingly. For the BN grains with plate-like shape, one may expect to get a larger grain size when the intersecting plane is parallel to the [110] direction, rather than normal to it, such as [001] direction. We may infer that the grain sizes obtained from DFIs after 4 h of milling are quite different in crystalline orientations from those after 9 h of milling. The former relates to more cross-sections parallel to [001] direction, or approximately parallel to it, while the latter probably depends on those that are in concordance with the [110] direction.

Unlike parameter \(k\), \(k^n\) is relatively difficult to be interpreted for its physical significance. Much of the argument lies in the unpredicted change of unit for \(k^n\) (Table 1). Normally, the unit of \((\text{nm})^1\) is used to scale for length, and \((\text{nm})^2\) for area. But what is the significance of \((\text{nm})^n\) when \(n\) is not an integer (e.g. \(0.5 < n < 1\) or \(1 < n < 1.5\))? And why are the values of \(k^n\) in good agreement with the results of XRD analysis in spite of the fact that they are apparently inconsistent in unit? This seems to be a paradox. However, the above analysis, in the authors’ view, has more significant meaning beyond this experiment itself. For example, the DFIs of BN powders are taken randomly after 9 h of milling but their results seem to be selective. (The obtained grain sizes in the majority seem to come from some specific or preferred crystalline orientation.) Whether this relates to the grain morphology or to other factors cannot be easily clarified. Is that a possibility that preferred orientation have occurred for BN grains during the last stage of milling (e.g. after 9 h of milling)? It is not rigorously exhibited in the diffraction pattern of TEM (Figure 5), although there are almost no (004) diffraction spots.

4. CONCLUSIONS

During the milling process, the grain size of hexagonal structure BN decreases rapidly but remains a monotonous plate-like shape, even when the grain size is less than 15 nm. An amorphization process may occur during the latter stage of milling as a consequence of the
Figure 7. Probability distribution as a function of grain size for BN powder milled for different time periods.

characteristics of the weak interlayer bonding of hexagonal structure BN. The grain size distributions of BN powders, different from conventionally normal or lognormal ones, have been studied in detail by using the Rosin-Rommler equation. The extrapolated parameters, such as $k^4$, indicate significant meaning about either the change of nanometer-sized BN grains or the ball milling process. It can be inferred that BN grains behave differently, at least in the aspect of crystalline orientations, during the early and late stages of ball milling.

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