Effect of ball-milling on dislocation generation and grain growth behavior in sintered NbC–Co

Dong-Yeol YANG,*,‡ Duk Yong YOON*,** and Suk-Joong L. KANG*,†

*Center for NanoInterface Technology, Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305–701, Republic of Korea
**Pohang University of Science and Technology, Pohang 790–784, Republic of Korea

Widely employed in the fabrication of structural ceramics, ball-milling is a process of mixing or pulverizing powders. Despite its popular use, the effects of ball-milling on grain growth behavior are nevertheless still obscure. In this study, we investigated the effects of ball-milling on grain growth behavior in light of the crystal growth theory in a model NbC–Co system with partially faceted grains. Two kinds of 90NbC–10Co (wt %) samples, with and without ball-milling, were prepared. With ball-milling, the density of dislocations increased considerably. In samples without ball-milling, abnormal grain growth (AGG) occurred from the beginning of liquid phase sintering at 1450°C. In contrast, in samples with ball-milling, grain growth behavior was quite normal and large abnormal grains did not appear up to 96 h of sintering. These observations can be explained in terms of the change in the critical driving force for appreciable growth with dislocation density. The present results also demonstrate that proper mechanical treatment (ball-milling) can be useful for suppressing AGG in cemented carbide systems.

Key-words : NbC–Co, Ball-milling, Dislocation, Abnormal grain growth, Liquid phase sintering

1. Introduction

The NbC–Co system has been a model carbide system for the study of grain growth and microstructural evolution in cemented carbides.1,8)–11) Previous studies of this system report different grain shapes and different grain growth behavior for different chemical compositions and temperatures.1,8)–7) Recent investigations on grain growth behavior in polycrystals show that the grain growth behavior is related to the shape of grains: abnormal for (partially) faceted grains and normal for rounded grains.8)–11) Some contradictory results in the NbC–Co system, however, may be related to the effects of ball milling when we consider the crystal growth theory.8)–10)11)

Ball milling is commonly employed in ceramic processing for the purpose of mixing or pulverizing powders. Widely used due to its simplicity, this process is performed by placing hard balls inside a jar along with the powder and a liquid, and then rotating the jar at an appropriate rate. The collisions between the particles and the balls during ball-milling can alter the size, distribution, degree of agglomeration, and dislocation density of the particles.12)–13) Among the initial state variables of powders, the dislocation density can affect grain growth during sintering.8)–14)

It is well documented that dislocations can significantly affect the growth rate of a crystal in a liquid matrix.15)–17) Theoretical analyses and experimental observations pertaining to the growth of faceted single crystals show that as the driving force increases, the rate of spiral growth at screw dislocations increases parabolically.15)–17) Recent investigations of grain growth also show a significant effect of dislocations.18)–22) Chung et al.19) observed that when SrTiO3 single crystals with different dislocation densities were embedded in a fine grained SrTiO3 powder with a liquid forming phase, crystals with a higher dislocation density grew faster than crystals with a low dislocation density. Similar results were also observed in Al2O3,21) BaTiO3,20) and PMN-PT.22) For metal systems, it was observed that small deformation enhanced the AGG rate.23) When a Cu specimen that exhibited stagnant grain growth was slightly deformed, AGG readily occurred. Under conditions where AGG occurred, a small deformation caused earlier formation of abnormal grains and more grains to grow abnormally. These results were attributed to an increased mobility of grain boundaries as a result of an increased dislocation density by deformation. The observed dislocation effects suggest that the step growth mechanism8)–11) is operative for the migration of faceted boundaries.

The purpose of this study is to identify the effects of ball-milling on dislocation generation and grain growth behavior in NbC–Co alloys. Two kinds of NbC–Co powder, mixed with and without balls, were prepared. The effects of ball-milling on powder characteristics and grain growth behavior were observed after powder mixing and sintering of powder compacts, respectively. It was found that ball-milling introduced dislocations in the interior and at the surface of NbC particles without appreciably changing the morphology and size of the particles. It was also found that ball-milling relieved abnormal grain growth behavior, which was attributed to an enhanced growth rate of grains by dislocations.

2. Experimental procedure

Commercial NbC (1.1 μm average size, Treibacher, Austria) and Co (0.8 μm average size, OMG, USA) powders of about 99.9 wt % purity were used to make specimens with a composition of 90NbC–10Co (wt %). The proportioned powder was mixed in a polyethylene bottle with ethanol for 24 h with and without WC–Co balls. The dried slurry was crushed in an agate
bowl and screened by being passed through a 100-mesh sieve. The mixed powder was lightly pressed into disks of 10 mm diameter and 2.5 mm thickness, and then cold isostatically pressed at 200 MPa. In order to prevent carbon loss during sintering, the powder compacts were packed with carbon black powder in a graphite crucible with a graphite cover and sintered at 1450°C under a vacuum of about 10⁻³ torr in a graphite furnace. The heating and cooling rates were approximately 20 and 33°C/min, respectively.

The sintered samples were vertically cut and polished up to a 1.0 μm finish. The microstructures of the samples were observed under optical and scanning electron microscopes after chemical etching in a Murakami solution [10 g K₃Fe(CN)₆ + 10 g NaOH + 100 g H₂O] for 20–60 s. The average grain size on a cross-section was measured by an image analyzer with software (Matrox Inspector 2.1). At least 300 grains were examined for each sample. Samples for transmission electron microscopy (TEM) (JEM-2100F, JEOL Ltd., Japan) were ultrasonically cut into 3 mm disks, mechanically ground to a thickness of 80 μm, dimpled to less than 5 μm, and finally ion-milled.

3. Results and discussion

Figure 1 shows the micrographs of milled NbC powders without and with WC–Co balls. In general, the effects of ball-milling on ceramic processing are known to be a reduction of particle size, mitigation of agglomeration, and introduction of dislocations. Comparing the sizes and morphologies of the mixed powders with and without balls, however, no remarkable differences were found. The average size (1.1 μm), size distribution, and degree of agglomeration were similar, as presented in Figs. 1(a) and 1(b).

Figure 2 shows typical TEM bright field images of dislocations in the NbC particles after milling. In the particle milled without WC–Co balls in Fig. 2(a), only a few dislocations are observed. In contrast, in the particle milled with WC–Co balls in Fig. 2(b), numerous dislocations are observed. This large difference in dislocation density was maintained even after sintering of the powder compacts at 1450°C, as shown in Fig. 3, indicating that the annealing out of dislocations at the sintering temperature was not significant and most of the disloca-
tions introduced by ball-milling remained during the sintering process.

The findings of previous investigations on the grain shape and grain growth behavior of NbC grains in a Co, Fe, or Ni matrix at temperatures close to 1400°C are somewhat conflicting. Sarian and Weart\textsuperscript{6} showed nearly cubic NbC grains in an NbC–Fe alloy (with about 20 wt % Fe) sintered at 1300°C, but the edges of the grains, particularly the small grains, were rounded. Warren\textsuperscript{1,2} also observed round-edged cube-shaped NbC grains in NbC–Ni and NbC–Co sintered at temperatures between 1380 and 1550°C. He contended that normal grain growth occurred in accordance with diffusion-controlled Ostwald ripening. In contrast, Oh et al.\textsuperscript{7} observed abnormal growth of cube-shaped NbC grains with fairly sharp edges in NbC–Fe samples prepared without ball-milling. A similar observation was also made in NbC–30Co (wt %) by Cho et al.\textsuperscript{4} At 1400°C, NbC grains were well faceted and AGG occurred. At 1820°C, however, the grain shape was mostly rounded and apparently normal grain growth occurred.

---

**Fig. 3.** Transmission electron micrographs of 90NbC–10Co (wt %) samples from milled powders (a) without and (b) with WC–Co balls. Samples sintered at 1450°C for 10 min. Many dislocations are present in the NbC grain interior in Fig. 3(b).

**Fig. 4.** Scanning electron micrographs of 90NbC–10Co (wt %) samples from powders milled without balls. Samples sintered at 1450°C for (a) 10 min, (b) 30 min, (c) 2 h, (d) 8 h, (e) 24 h, and (f) 96 h.
with an invariant relative grain size distribution. In an experiment at 1400°C, Moon et al.3) observed AGG in NbC–30Co (wt %) and NbC–20Co (wt %) samples prepared without ball milling and apparently normal grain growth behavior in the samples with ball-milling. The experimental observations thus far suggest that the grain growth behavior is largely affected by the shape of grains and mixing method of powders.

Figure 4 shows micrographs of 90NbC–10Co (wt %) samples sintered at 1450°C for various times (10 min–96 h) after milling without balls. At the early stage of sintering (10 min), the average size of NbC grains is \( \bar{7} \mu m \) and the microstructure is quite uniform. After 30 min of sintering, abnormal grains suddenly appear. With increasing sintering time, the abnormal grains, whose shape is quite well faceted, grew very rapidly. As shown by the abnormal grains in the sample sintered at 1450°C for 96 h [Fig. 4(f)], the NbC grains are cubic with slightly rounded edges.

Figure 5 shows the micrographs of 90NbC–10Co (wt %) samples sintered at 1450°C for various times (10 min–96 h) after milling with balls. The grain shape of the ball-milled samples is similar to that of the samples mixed without balls. However, with ball-milling, the growth behavior of NbC grains changed from abnormal to quite-normal (pseudo-normal) up to 96 h of sintering. Figure 6 plots the measured grain size distributions normalized to the average size for the samples milled without and with balls. The measurement confirms a large difference in grain growth behavior between the samples milled without and with balls, i.e., abnormal and quite normal, respectively. For the samples milled with balls, however, the relative grain size distribution tends to broaden as the sintering time increases [Fig. 6(b)].

Abnormal growth of faceted grains in a liquid matrix has been observed in a number of systems.4),23)–30) Abnormal grain growth in faceted systems is attributed to the nonlinear growth rate of faceted grains with respect to the driving force.9),11),23),24),29) The observed effects of ball-milling can also be explained using the schematic illustration in Fig. 7 based on the crystal growth theory.8),14) For grains with a very low dislocation density, as in the case for the sample milled without balls, the growth is governed either by the formation of 2-dimensional nuclei and their growth (2DNG) or dislocation-assisted growth (DAG).8),13),14),28) In the case of 2DNG, the growth rate is an exponential function of the driving force, showing a critical driving force for appreciable growth. In the case of screw dislocation-assisted growth, the growth rate is proportional to the square of the driving force. In both cases, the driving force for appreciable growth of the grain is large, as schematically shown by curve A in Fig. 7. For grains with a very high dislocation density, the growth is governed by dislocation-assisted growth.
The growth rate increases as the dislocation density increases, as shown by curve B in Fig. 7. The growth rate for 2DNG or DAG, however, becomes linear with respect to the driving force when the growth rate governed by 2DNG (or DAG) becomes faster than the growth rate governed by the diffusion of atoms through the matrix, schematically shown as a straight line in Fig. 7.

In a sample with numerous grains of different sizes, each grain has its own driving force for growth or dissolution. There is a range of driving force from −∞ for an infinitesimal sized grain to a maximum value, Δg<sub>max</sub>, for the largest grain in the sample, as schematically shown in Fig. 7. Only a small number of grains can grow relatively fast compared with other grains, if Δg<sub>max</sub> is slightly larger than or comparable with the driving force for the transition between interface reaction control and diffusion control. This corresponds to the case of AGG in the sample milled without balls. In contrast, in the sample with high dislocation densities as a result of ball milling, a large number of grains can grow appreciably, showing pseudo-normal grain growth. As grain growth proceeds, however, Δg<sub>max</sub> decreases and the number of grains having driving forces larger than a critical value decreases. The grain size distribution tends to broaden and abnormal grains can appear, as seen in Fig. 6.

The present investigation demonstrates that the grain growth behavior in a NbC–Co system with round-edged cube grains can vary considerably with ball milling. The major effect of ball-milling is found to be the introduction of dislocations in the grain boundary. With the introduction of dislocations by ball-milling, grain growth behavior can change from abnormal to quite normal. Some contradictory results of grain growth behavior in the NbC–Co system<sup>1,4,6,7</sup> can thus be explained by considering the effect of dislocations.

### 4. Conclusions

The effects of ball-milling on grain growth behavior were studied for a model carbide system, NbC–Co. For the studied experimental conditions, ball-milling did not decrease the average size but increased the dislocation density at the surface of NbC particles. With the introduction of dislocations by ball-milling, the grain growth behavior changed from abnormal to quite normal in 90NbC–10Co (wt %) alloys. This change in grain growth behavior can be explained by the previously suggested principles of microstructural evolution<sup>10,11</sup> in conjunction with the dislocation-assisted crystal growth theory. Ball-milling was found to effectively suppress AGG in NbC–Co.

### Acknowledgement

This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0031407).

### References