

Properties and Rapid Consolidation of Binderless Nanostructured NbC by Pulsed Current Activated Sintering

Byung-Ryang Kim,¹ Min-Seok Moon,^{1,2} Kee-Do Woo,^{1,2} and In-Jin Shon^{1,2,*}

¹Division of Advanced Materials Engineering and the Research Center of Advanced Material Development, Engineering College, Chonbuk National University, Jeonju-si, Jeonbuk 561-756, Korea

²Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, Jeonju-si, Jeonbuk 561-756, Korea

A dense nanostructured NbC hard material with a relative density of up to 98% was produced within 2 minutes from a mechanically activated powder by the simultaneous application of a pressure of 80 MPa and a pulsed current corresponding to 2800 A. With increasingly fine initial NbC powder size, accordingly higher density and superior mechanical properties were obtained. The fracture toughness and hardness values obtained were $6.0 \text{ MPa}\cdot\text{m}^{1/2}$ and 2134 kg/mm^2 , respectively.

Keywords: Sintering, Nanostructured material, Carbides, Hardness, Toughness, NbC.

1. INTRODUCTION

Metal carbides have been used for optical coatings, electrical contacts, and diffusion barriers^[1] due to their optical, electronic, and magnetic properties. Among these carbides, niobium carbide is a very important material with promising properties, such as outstanding hardness, a high melting point (3610°C), good resistance to chemical attack, good catalytic properties, and excellent electronic conductivity.^[2-4] Therefore, it can find applications in many fields, such as mechanical, chemical, and microelectronic industries.

Offering wide functional diversity and exhibiting enhanced or different properties compared with bulk materials, nanostructured materials have been widely investigated.^[5,6] In particular, in the case of nanostructured ceramics, the presence of a large fraction of grain boundaries can lead to unusual or better mechanical, electrical, optical, sensing, magnetic, and biomedical properties.^[7-13] Recently, nanocrystalline powders have been developed by co-precipitation, a thermochemical and thermomechanical process referred to as the spray conversion process (SCP), and high energy milling.^[14,15] The grain size in sintered materials, however, becomes substantially larger than that in pre-sintered powders due to fast grain growth during the conventional sintering process. Even if the initial particle size is less than 100 nm, the grain size increases rapidly up to 500 nm or larger during conventional sintering.^[16] Therefore, controlling grain growth during sintering is one of the keys to commercial

success of nanostructured materials. In this regard, the pulsed current activated sintering method, whereby dense materials can be fabricated within 2 min, has been shown to be effective in achieving this goal.^[17]

The sintering temperature of a high energy mechanically milled powder is lower than that of an unmilled powder, due to an increase in the reactivity, internal and surface energy, and surface area of the former, which all contribute to its so-called mechanical activation.^[18-20]

In this work, we investigated the fabrication of a nanopowder and the sintering of NbC by the PCAS method without the use of a binder. In addition, we also studied the effect of ball milling on the sintering behavior and mechanical properties of binderless NbC.

2. EXPERIMENTAL PROCEDURE

Niobium carbide powder with 99% purity and a grain size of $<10 \mu\text{m}$ was supplied by Alfa Company. The powder was first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for various periods of time (0, 1, 4, 10 hr). Tungsten carbide balls (8.5 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of balls-to-powder was 30:1. Milling resulted in a significant reduction of the grain size. The powder size of NbC decreased with increasing milling time, as shown in Fig. 1. The grain size of the NbC was calculated from the full width at half-maximum (FWHM) of the diffraction peak by C. Suryanarayana and M. Grant Norton's formula.^[21] The average grain sizes of the NbC

*Corresponding author: ijshon@chonbuk.ac.kr

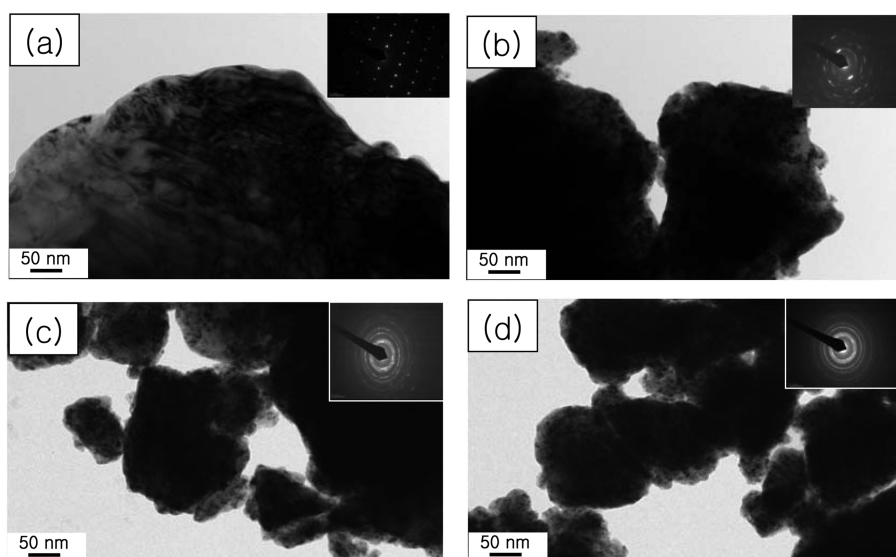


Fig. 1. TEM micrographs of the pure NbC powder with milling times of: (a) 0 h, (b) 1 h, (c) 4 h, and (d) 10 h.

milled for 1 h, 4 h, and 10 h determined by C. Suryanarayana and M. Grant Norton's formula were about 33 nm, 25 nm, and 21 nm, respectively.

After milling, the powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the PCAS apparatus.^[17] The PCAS apparatus includes a 30 kW power supply that provides a pulsed current (on time = 20 μ s, off time = 10 μ s) through the sample and applies a uniaxial pressure of 50 kN. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. The induced current was then activated and maintained until the densification rate was negligible, as indicated by the real-time output of the shrinkage of the sample. The shrinkage was determined by a linear gauge measuring the vertical displacement. The temperatures were measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the induced current was turned off and the sample was cooled to room temperature. The process was carried out under a vacuum of 4×10^{-2} Torr.

The relative density of the sintered sample was measured by the Archimedes method. Microstructural information was obtained from product samples, which had been polished and etched using Murakami's reagent (10 g potassium ferricyanide, 10 g NaOH, and 100 mL water) for 1 min at room temperature. Compositional and microstructural analyses of the products were performed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS).

3. RESULTS AND DISCUSSION

The variations of the shrinkage displacement and temper-

ature with heating time for 2800 A during sintering via high energy ball milled WC under a pressure of 80 MPa are shown in Fig. 2. In all cases, thermal expansion occurred with the application of pulsed current, and shrinkage thereafter increased due to consolidation. The shrinkage initiation temperature varied from 800°C to 1300°C depending on the milling time. The temperature at which shrinkage started

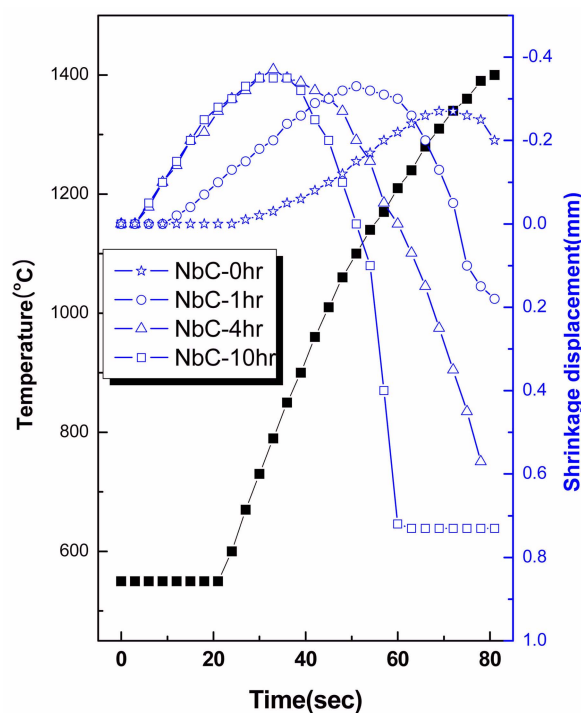


Fig. 2. Variations of temperature and shrinkage with heating time during sintering of the binderless NbC powder with milling times of 0 h, 1 h, 4 h, and 10 h.

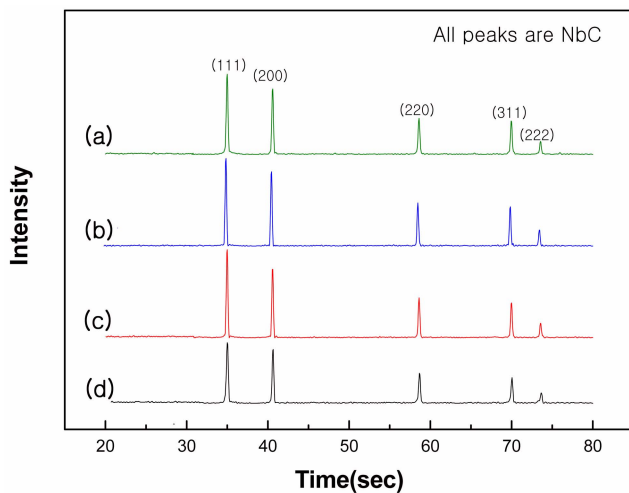


Fig. 3. XRD patterns of the binderless NbC obtained by sintering various milled powders: (a) 0 h, (b) 1 h, (c) 4 h, and (d) 10 h.

decreased with increasing milling time, and the high energy ball milling affected the rate of densification and the final density. The sintering temperature of the high energy mechanical milled NbC is lower than that of the unmilled powder, due to increases in the reactivity, internal and surface energy, and surface area of the powder, which all contribute to its mechanical activation.^[18-20]

Figure 3 shows the XRD patterns of the NbC after sintering for all four powders used in this work. Only NbC phase is present. The full width at half-maximum (FWHM) of the diffraction peak in the sintered NbC increased with increasing milling time, due to grain refinement. The average grain

sizes of the NbC heated to 1330°C, as calculated by C. Suryanarayana and M. Grant Norton's formula, were roughly 466 nm, 235 nm, 139 nm, and 76 nm for the samples with milling times of 0 h, 1 h, 4 h, and 10 h, and their corresponding relative densities were approximately 89%, 95%, 96%, and 98%, respectively.

Figures 4 and 5 show the effects of the ball milling time on the microstructure of the NbC sintered under a pressure of 80 MPa and a pulsed current corresponding to 2800 A. From Fig. 5, it is seen that NbC consists of a nanophase.

It is believed that the rapid sintering of the highly dense, binderless NbC by PCAS can be explained as follows. The role played by the pulsed current has been variously interpreted, with the effect being explained in terms of the fast heating rate due to Joule heating, the presence of a plasma in the pores separating the powder particles, and the intrinsic contribution of the current to the mass transport.^[22-25]

Vickers hardness measurements were performed on polished sections of the NbC samples using a load of 10 kg_f and a dwell time of 15 s. Indentations with sufficiently large loads produced radial cracks emanating from the corners of the indent. The length of these cracks permits the fracture toughness of the material to be estimated using Anstis' expression.^[26] The Vickers hardnesses of the NbC samples ball milled for 1 h, 4 h, and 10 h were 1154 kg/mm², 1576 kg/mm², and 2134 kg/mm², and their fracture toughnesses were 8 MPa·m^{1/2}, 7 MPa·m^{1/2}, and 6 MPa·m^{1/2}, respectively. These values represent the averages of ten measurements, respectively. The hardness of the NbC was remarkably increased by refinement of the grain size, without a significant decrease of the fracture toughness.

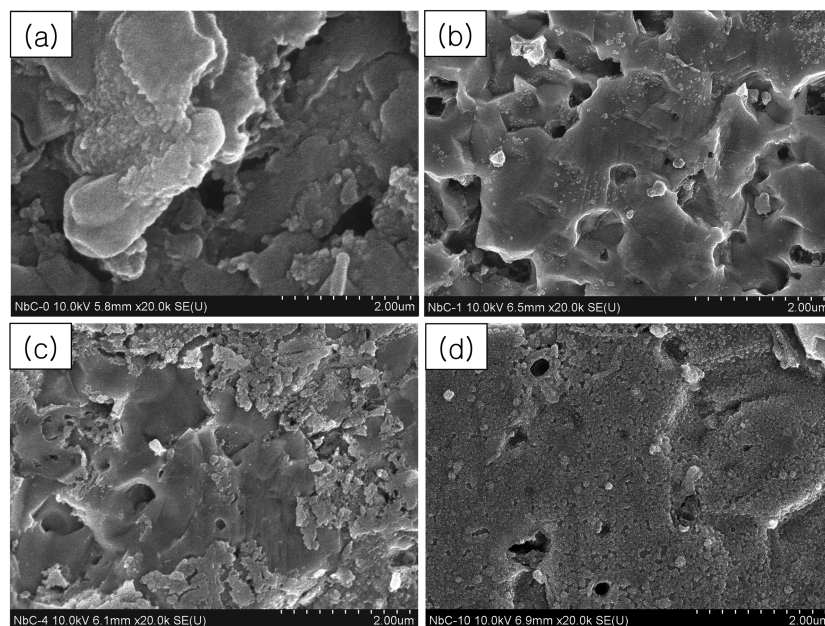


Fig. 4. FE-SEM micrographs of pure NbC obtained by sintering various milled powders: (a) 0 h, (b) 1 h, (c) 4 h, and (d) 10 h.

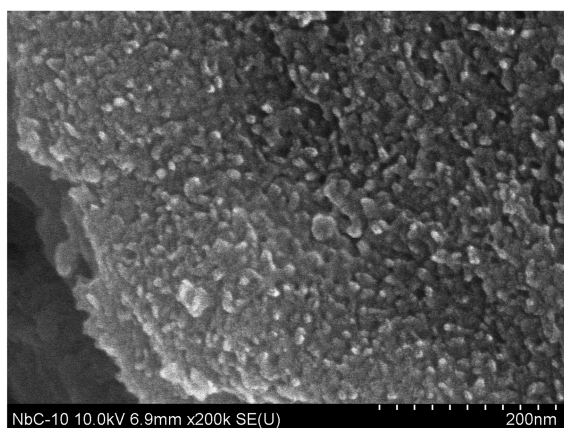


Fig. 5. FE-SEM micrographs of the pure NbC obtained by sintering the 10 h milled powder.

4. SUMMARY

A nanopowder was fabricated by high energy ball milling. A dense nanostructured NbC was obtained within 2 min from a mechanically activated NbC powder by pulsed current activated sintering. The sintering temperature of the high energy mechanically milled NbC was lower than that of the unmilled powder. The relative densities of the NbC samples with milling times of 0 h, 1 h, 4 h, and 10 h were approximately 89%, 95%, 96%, and 98%, respectively. The Vickers hardness and fracture toughness of the NbC obtained from the milled powder by sintering for 10 h were 2134 kg/mm^2 and $6.0 \text{ MPa m}^{1/2}$, respectively.

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REFERENCES

1. S. T. Oyama, *Introduction to the Chemistry of Transition Metal Carbides and Nitrides* (ed., S. T. Oyama), Blackie Academic and Professional (1996).
2. T. Amriou, B. Bouhafs, H. Aourag, B. Khelifa, S. Bresson, and C. Mathieu, *Phys. B : Condens. Matter* **325**, 46 (2003).
3. M. Nagai, T. Miyao, and T. Tsuboi, *Catal. Lett.* **18**, 9 (1993).
4. E. V. Pechen, S. I. Krasnosvobodtsev, N. P. Shabanova, E. V. Ekimov, A. V. Varlashkin, and V. D. Nozdrin, *Physica. C* **235**, 2511 (1994).
5. H. Gleiter, *Nanostruct. Mater.* **6**, 3 (1995).
6. J. R. Yoon, D. J. Choi, K. H. Lee, J. Y. Lee, and Y. H. Kim, *Electron. Mater. Lett.* **4**, 167 (2008)
7. J. Karch, R. Birringer, and H. Gleiter, *Nature* **330**, 556 (1987).
8. A. M. George, J. Iniguez, and L. Bellaiche, *Nature* **413**, 54 (2001).
9. D. Hreniak, and W. Streck, *J. Alloy. Compd.* **341**, 183 (2002).
10. C. Xu, J. Tamaki, N. Miura, and N. Yamazoe, *Sensor. Actuat. B-Chem.* **3**, 147 (1991).
11. D. G. Lamas, A. Caneiro, D. Niebieskikwiat, R. D. Sanchez. D. Garcia, and B. Alascio, *J. Magn. Magn. Mater.* **241**, 207 (2002).
12. C. Nahm, C. Kim, Y. Park, B. Lee, and B. Park, *Electron. Mater. Lett.* **4**, 5 (2008).
13. E. S. Ahn, N. J. Gleason, A. Nakahira, and J. Y. Ying, *Nano Letters.* **1**, 149 (2001).
14. Z. Fang and J. W. Eason, *Int. J. Refract. Met. H. Mater.* **13**, 297 (1995).
15. A. I. Y. Tok, L. H. Luo, and F. Y. C. Boey, *Mater. Sci. Eng. A* **383**, 229 (2004).
16. M. Sommer, W.D. Schubert, E. Zobetz, and P. Warbichler, *Int. J. Refract. Met. H. Mater.* **20**, 41 (2002).
17. I. Y. Ko, B. R. Kim, K. S. Nam, B. M. M, B. S. Lee, and I. J. Shon, *Met. Mater. Int.* **15**, 399 (2009).
18. F. charlot, E. Gaffet, B. Zeghmami, F. Bernard, and J. C. Liepce, *Mater. Sci. Eng. A* **262**, 279 (1999).
19. V. Gauthier, C. Josse, F. Bernard, E. Gaffet, and J. P. Larpin, *Mater. Sci. Eng. A* **262**, 117 (1999).
20. M. K. Beyer and H. Clausen-Schaumann, *Chem. Rev.* **105**, 2921 (2005).
21. C. Suryanarayana and M. Grant Norton, *X-ray Diffraction A Practical Approach*, p. 207, Plenum Press, New York (1998).
22. Z. Shen, M. Johnsson, Z. Zhao, and M. Nygren, *J. Am. Ceram. Soc.* **85**, 1921 (2002).
23. J. E. Garay, U. Anselmi-Tamburini, Z. A. Munir, S. C. Glade and P. Asoka-Kumar, *Appl. Phys. Lett.* **85**, 573 (2004).
24. J. R. Friedman, J. E. Garay. U. Anselmi-Tamburini, and Z. A. Munir, *Intermetallics* **12**, 589 (2004).
25. J. E. Garay, J. E. Garay. U. Anselmi-Tamburini, and Z. A. Munir, *Acta Mater.* **51**, 4487 (2003).
26. G. R. Anstis, P. Chantikul, B. R. Lawn, D. B. Marshall, *J. Am. Ceram. Soc.* **64**, 533 (1981).