Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 585–591

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

High-frequency induction heated sintering of High-energy ball milled $TiC_{0.5}N_{0.5}$ powders and mechanical properties of the sintered products

Wonbaek Kim[a], Chang-Yul Suh[a], Ki-Min Roh[a], Jae-Won Lim[a], Sujeong Lee[a], Song-Lee Du[b], In-Jin Shon[b,*]

[a]*Minerals and Materials Processing Division, Korea Institute of Geoscience, Mining and Materials Resources, Daejeon, Republic of Korea*
[b]*Division of Advanced Materials Engineering and the Research Center of Advanced Materials Development, Engineering College, Chonbuk National University, 561-756, Republic of Korea*

Received 28 May 2012; received in revised form 10 June 2012; accepted 11 June 2012
Available online 5 July 2012

Abstract

Commercial $TiC_{0.5}N_{0.5}$ powders were high-energy ball milled for various durations and consolidated without binder using the high-frequency induction heated sintering method (HFIHS). The effect of milling on the sintering behavior, crystallite size and mechanical properties of TiCN powders were evaluated. A nanostructured dense TiCN compact with a relative density of up to 98% was readily obtained within 3 min. The ball milling effectively refined the crystallite structure of TiCN powders and facilitated the subsequent densification. The sinter-onset temperature was reduced appreciably by the prior milling for 10 h from 1170 °C to 820 °C. Accordingly, the relative density of TiCN compact increased as the milling time increases. The microhardness of sintered TiCN was linearly proportional to the density while its toughness did not show any correlation with the crystalline size or density. It is clearly demonstrated that a quick densification of nano-structured TiCN bulk materials to near theoretical density could be obtained by the combination of HFIHS and the preparatory high-energy ball milling processes.

Keywords: Nanomaterials; A. Sintering; C. Hardness; Fracture toughness

1. Introduction

TiCN is one of the promising ceramic materials, because it exhibits unusual combinations of physical and chemical properties such as high hardness, high melting point and excellent resistance to oxidation [1,2]. Industrial applications of the compound are in cutting tools and hard coatings. It is used extensively in cutting tool and abrasive materials in composite with a binder metal, such as Ni. The binder phase has inferior chemical characteristics compared to the carbide or nitride phase. Most notably, corrosion and oxidation occur preferentially in the binder phase [3]. Hence, the development of binderless TiCN is needed for water jet nozzle, mechanical seals and sliding parts due to their enhanced corrosion resistance and hardness.

Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties. Since nanomaterials possess high strength, high hardness, relatively good ductility and toughness, undoubtedly, more attention has been paid to the application of nanomaterials [4–6]. In recent days, nanocrystalline powders have been developed by the thermochemical and thermomechanical process named the spray conversion process (SCP), co-precipitation and high energy milling [7–9]. However, the grain size in sintered materials becomes much larger than that in pre-sintered powders due to the rapid grain growth during a conventional sintering process. So, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. Unconventional

*Corresponding author. Tel.: +82 63 270 2381; fax: +82 63 270 2386.
E-mail address: ijshon@chonbuk.ac.kr (I.-J. Shon).

0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.06.068

sintering techniques, including high-pressure densification, magnetic pulse compaction and shock densification, have been proposed to overcome the problem of grain growth [10]. However, these methods have failed to provide fast, reproducible techniques that yield large quantities of high density samples with nanostructured grains.

The high-frequency induction heated sintering (HFIHS) method recently emerged as an effective technique for sintering and consolidating high temperature materials [11,12]. HFIHS is similar to traditional hot-pressing, but the sample is heated by a induced electric current that flows through the sample and a die. This process increases the heating rate (up to 2000 °C/min) to a degree much higher than that of traditional hot-press sintering.

In this study, we investigated the binderless sintering behavior of TiCN using the HFIHS method. The effect of milling duration on the densification behavior, crystallite size and mechanical properties of TiCN powders were evaluated.

2. Experimental procedures

The TiCN powder used in this research was supplied by Treibacher Industrie AG (Germany). The average particle size was about 1.4 μm and the purity was 99%. The composition of C and N was 10.64 and 10.88 wt%, respectively. Oxygen was 0.24 wt%. The powder was first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for various time periods (0, 1, 4, and 10 h). Tungsten carbide balls (9 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 in the particle size. The crystallite size of TiCN powders was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton's formula [13]

$$B_r(B_{crystalline}+B_{strain})\cos\theta = k\lambda/L+\eta\sin\theta \quad (1)$$

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after instrumental correction; $B_{crystalline}$ and B_{strain} are FWHM caused by small grain size and internal stress, respectively; k is a constant (with a value of 0.9); λ is wavelength of the X-ray radiation; L and η are the grain size and internal strain, respectively; and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship: $B=B_r+B_s$, where B and B_s are the FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.

The powders were placed in a graphite die (outside diameter 45 mm, inside diameter 20 mm, height 40 mm) and introduced into the high-frequency induction heated sintering (HFIHS) apparatus shown schematically in Fig. 1. The HFIHS apparatus includes a 15 kW power supply which provides an induced current through the sample under 50 kN uniaxial load. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. An induced current was then activated and maintained

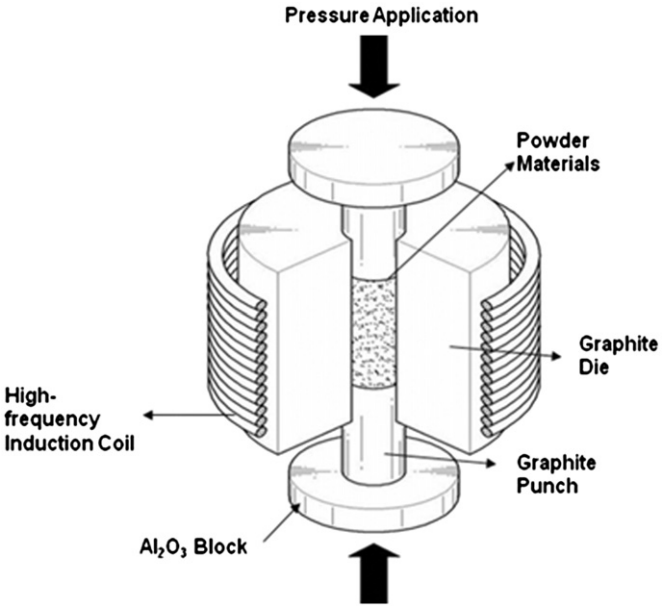

Fig. 1. Schematic diagram of the apparatus for the high-frequency induction heated sintering (HFIHS).

until the densification rate became negligible according to the real-time output of the sample shrinkage. The shrinkage was measured by a linear gage which shows the vertical displacement. 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 cooled to room temperature. The process was carried out under a vacuum of 4×10^{-2} Torr (5.33 Pa).

The relative density of sintered sample was measured by the Archimedes method. Microstructural information was obtained from the surface of the samples, which were polished and etched using Murakami's reagent (10 g potassium ferricyanide, 10 g NaOH, and 100 mL water) for 1–2 min at room temperature. Compositional and microstructural analyses of the products were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and field emission scanning electron microscope (FE-SEM). Vickers hardness was measured at a load of 10 kg_f and a dwell time of 15 s.

3. Results and discussion

3.1. Effect of milling on crystallite size

The high-energy milling refined the microstructure of TiCN particles. Fig. 2(a–d) shows X-ray diffraction patterns of the TiCN powders after milling for 1–10 h. The broadening of TiCN peaks due to crystallite refinement is evident after milling for 1 h, and it continuously broadened during the prolonged milling. The milling process is known to introduce impurities from the ball and/or container. However, in this study, peaks other than TiCN were not identified. SEM images of Fig. 3(a–d) shows the particle size reduction occurred during the high-energy milling process. The TiCN