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ScienceDirect
Journal of the European Ceramic Society 31 (2011) 809–813
www.elsevier.com/locate/jeurceramsoc

Spark plasma sintering of TiCN nanopowders in non-linear heating and loading regimes

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Received 5 July 2010; received in revised form 15 November 2010; accepted 28 November 2010
Available online 17 December 2010

Abstract

Consolidation of commercially available nanostructured titanium carbonitride (TiCN) powder has been performed by Spark Plasma Sintering (SPS) in the temperature range from 1300 to 1600 °C. The effect of non-linear heating and loading regimes on consolidation of high melting point nanocomposites has been investigated. SPS consolidated TiCN material has demonstrated near fully dense and fine homogeneous microstructure with average grains size about 150 nm. Nanohardness and fracture toughness of the TiCN nanocomposite have been measured as 33 ± 0.9 GPa and 3.2 MPa $m^{1/2}$ respectively.

Keywords: SPS/FAST; Nanocomposites; Microstructure

1. Introduction

Spark plasma sintering (SPS) is a widely recognized field assisted sintering technique (FAST), enabling quite rapid consolidation of desired materials, in a range of 2–15 min for a run including soaking time. High rate consolidation of various metals and ceramics during the SPS process makes this method attractive for the production of nanostructured materials.[1–6] In the SPS process, materials are subjected simultaneously to a very fast heating, usually with heating rates in the range from 100 to 600 °C/min, and to pressure loading up to 100–200 MPa, followed by a 1–3 min soak at maximum temperature. This results in obtaining high relative density (95–98%) of the consolidated materials at temperatures, which are generally 150–200 °C lower compared to the maximum processing temperatures for conventional sintering or hot pressing techniques.[1,3,6] In spite of the fact that SPS has been extensively investigated over the past decades, the effect of heating rate and pressure on the consolidation of various materials is still under the investigation. The development of novel technological approaches for SPS leading toward the improvement of final material properties and microstructure is still required.

At pressureless sintering, the most effective way to control microstructure during densification is to control the heating rate based on the current material's densification rate. This phenomenological model was implemented to a rate-controlled sintering (RCS) technique and was successfully used for consolidation of different types of nanocrystalline or submicron materials such as TiN, AlN, $BaTiO_3$, ZrO_2 etc.[7–9] On the other hand, the main advantage of SPS is the combination of very high heating rates with high pressure permitting consolidation of different materials much faster and without significant grain growth.[1–3,6,10] In this work, we applied the RCS technology[7] to the SPS consolidation method in order to investigate the influence of non-linear heating and loading regimes on TiCN microstructure formation. TiCN nanopowder was selected as a sample material due to its commercial availability and due to the fact that parts fabricated from TiCN-based composites are widely used in industry. For example, additive-free titanium carbonitride-based bulk nanocomposites are the most promising materials for cutting tools due to their increased hardness (up to 30–32 GPa), high wear resistance, high edge strength and edge sharpness.[2]

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doi:10.1016/j.jeurceramsoc.2010.11.030

Table 1
Characteristics of nanopowder.

Materials formula	$TiC_{0.5}N_{0.5}$
Producer	Nanostructure & Amorphous Materials Inc.
$d_{aver.}$, nm (±3%)	80/61
Lattice constant (nm)	0.4291 ± 0.0001
Specific surface area (m^2/g)	25
[O] (wt.%)	<1

$d_{aver.}$, average particle size estimated by laser granulometry/XRD.

2. Material and methods

Commercially available titanium carbonitride nanopowder (Nanostructure and Amorphous Materials Inc., Nanoamor, USA) was used to evaluate the influence of heating rate and pressure on its sinterability and to develop a non-linear consolidation regime for the SPS technique. The initial powder properties of the TiCN nanopowder are summarized in Table 1, while the powder morphology observed by TEM is shown in Fig. 1.

SPS experiments were conducted in an SPS apparatus manufactured by FCT Systems GmbH (maximal temperature = 2400 °C, pressing force up to 250 kN, maximal current = 8000 A, maximal voltage = 10 V, media: vacuum – 5×10^{-2} mbar, nitrogen). All of these parameters were closely monitored during the experiments. The densification of nanopowders during the SPS consolidation process was monitored as a travel distance of an upper piston (a bottom piston was fixed) and recalculated later on to a corresponding relative density of the specimens.

About 15 g of TiCN nanopowder was loaded into a 30 mm diameter graphite die with punches followed by application of 50 MPa uniaxial pressure to establish a good electrical contact between TiCN particles and between the graphite instrument and the powder. Two types of SPS consolidation regimes were tested. The first one was a single-stage regime ($P = 50$ MPa or 70 MPa load, heating rate 200 °C/min, $T_{max} = 1600$ °C without isothermal soak), and the second one was a multiple-stage regime (non-linear) with sequential increase of pressure from 50 to 70 MPa and simultaneous decrease of heating rate from 100 °C/min to 20 °C/min. A pulse electric current with 20 ms pulse rate and 1 ms pause between pulses was applied to the samples during the SPS process. A temperature of the inner surface of the upper graphite piston was monitored by a digital pyrometer. The SPS consolidation regimes used in the experiments are summarized in Fig. 2. No isothermal soak at the maximum temperature was used in order to avoid uncontrolled grain growth.

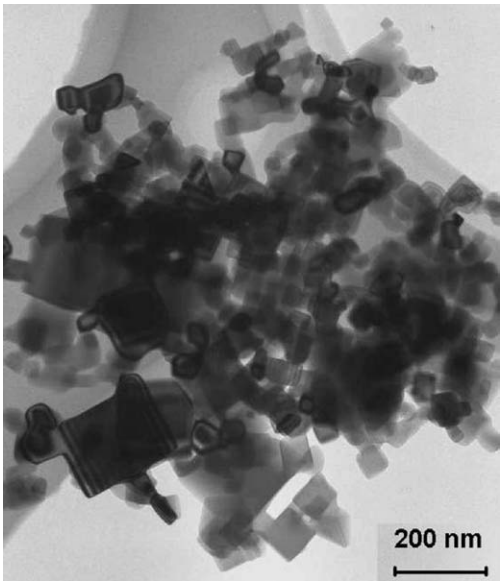

Fig. 1. TEM micrograph of the investigated TiCN powder.

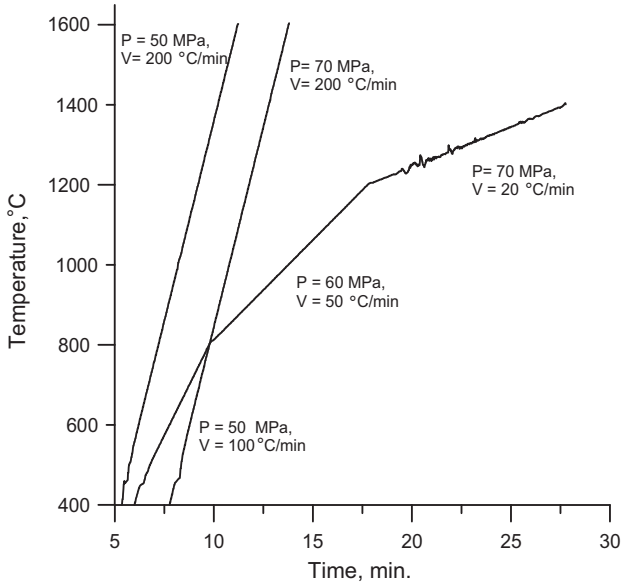

Fig. 2. SPS regimes of TiCN nanopowder consolidation.

3. Characterization

The final density of the SPS consolidated materials were measured by Archimedes method in deionised water at room temperature. The X-ray diffraction method (XRD) was used for the qualitative phase analysis (XRD-7 with Cu Kα radiation, Seifert-FPM, Freiberg, Germany). The crystallite size was calculated using Scherrer formula. Additionally, the particle size distribution of TiCN nanopowders was estimated by a light scattering particle size analyzer (Zetasizer 1000 HS, Malvern Instruments, United Kingdom) and by a transmission electron microscope (JEOL JEM-2100F, Japan). Vickers hardness and fracture toughness of sintered composite ceramics were measured at 50 g and 10 kg load conditions by PMT-3 (LOMO, Russia) and MMT-3 (Buehler, USA) hardness testers. Nanohardness of consolidated nano-TiCN was measured by a "Micron-Gamma" (National Aviation University, Ukraine) nanohardess tester with Berkovich indenter under 10 g and 20 g load conditions. Microstructure of the polished surface of sintered composites was examined by a Field Emission Scanning Electron Microscopy NVision 40 (Carl Zeiss SMT AG, Germany).

4. Results and discussion

4.1. Densification of TiCN nanopowders

Among various parameters of the SPS process, temperature, heating rate and pressure are the most suitable process parameters, control of which leads to achievement of the desired density and microstructure of consolidated materials. The relationship between densification and heating rate for pressureless sintering has been elucidated in the rate-controlled sintering theory.[7] The main idea is to control the consolidation process via the estimation of suitable densification rate and maintaining it stable during the whole consolidation process. Both grain size and final density of the material are used as control parameters. Generally, the time–temperature schedule of the RCS consists of three stages: (i) initial stage with high heating rate, when about 75% of the material's density is achieved; (ii) intermediate stage when the heating rate is partially decreased, and (iii) final stage with slowest heating rate.

Formally, SPS and hot pressing are the two comparable processes, the kinetic of which could be described by the following equation written in a simplified version[11]:

$$\frac{1}{D}\frac{dD}{dt} = \frac{B\phi\mu_{eff}b}{kT}\left(\frac{b}{G}\right)^{p}\left(\frac{\sigma_{eff}}{\mu_{eff}}\right)^{n} \quad (1)$$

where D is an instantaneous relative density, t is a time, b is a Burgers vector, Φ is a diffusion coefficient, B is a constant, G is a grain size, σ_{eff} is an instantaneous effective stress acting on the powder bed and μ_{eff} is an instantaneous shear modulus of the powder bed. As a sequence, the densification rate is a function of the compaction pressure and temperature. So, it is possible to control the material microstructure by keeping the material densification rate under control.

First of all, the influence of applied pressure on TiCN nanopowder densification has been estimated. A few preliminary runs up to 1600 °C with either 50 MPa or 70 MPa load and 200 °C/min constant heating rate have been performed (Fig. 2). Such high heating rate was purposely selected to estimate the influence of pressure on the densification process. In both cases, the densification has started at 1000 °C, while the maximum densification rate has been reached at 1270 °C and 1380 °C for the materials processed with 70 MPa and 50 MPa loads, respectively (Figs. 3 and 4). The densification of TiCN nanopowder under 70 MPa load condition has been completed at 1470 °C with 94% of theoretical density achieved (Fig. 4, curve 1). On the other hand, TiCN consolidated at 50 MPa has demonstrated twice higher densification rate with the densification completion at 1520 °C (curve 2, Fig. 4). In both cases, extension of heating process above 1500–1550 °C, when $(1/D)(dD/dt) \rightarrow 0$, resulted only in minor densification and leaded to a higher probability of material failure (cracking and damage). So, in order to get more uniform densification, it is preferable to begin the consolidation process at 50 MPa load followed by a gradual load increase up to 70 MPa. This should support stable densification rate up to about 1400 °C. The SPS heating profile should be also modified in order to accommodate all of the advantages of the RCS

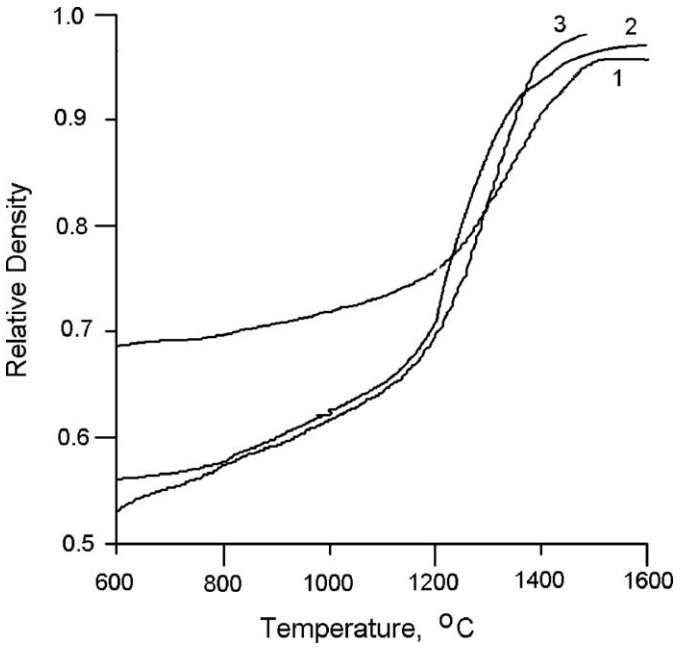

Fig. 3. Relative density of nanostructured TiCN as a function of the sintering temperature: (1) one step SPS $P = 70$ MPa in vacuum, $V = 200$ °C/min; (2) one step SPS $P = 50$ MPa in vacuum, $V = 200$ °C/min; (3) few step SPS in vacuum.

theory. The new variable heating rate profile was designed as follow: 100 °C/min heating rate at the beginning of the process, 50 °C/min heating rate at the intermediate stage and 20 °C/min at the final stage of sintering. The first heating rate switching point T_1 was selected at 800 °C, which was the temperature for densification onset at 50 MPa load condition. The second heating rate switching point T_2 was selected at 1200 °C. Generally, slow heating rates at the final stage of consolidation promote further densification of materials without significant grain growth.

Densification kinetic of TiCN nanopowder under different SPS regimes is presented in Figs. 3 and 4. Comparing two types of SPS regimes, the single-stage and the multiple-stage regimes, it is obvious that the multiple-stage regime requires significantly more time to achieve the same density of consoli-

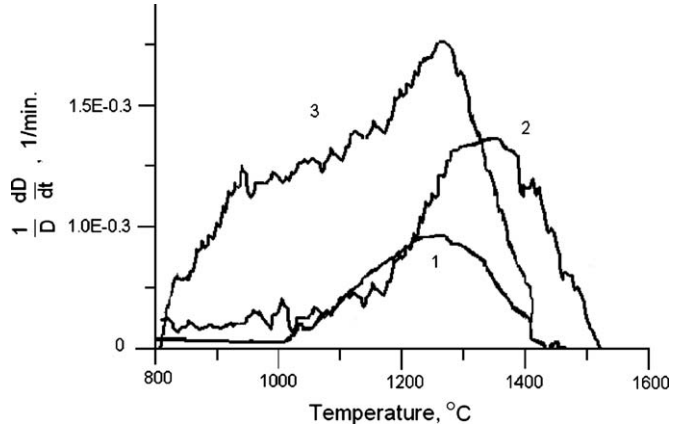

Fig. 4. Densification rate curves for nanostructured TiCN consolidated in vacuum: (1) one step SPS $P = 70$ MPa, $V = 200$ °C/min; (2) one step SPS $P = 50$ MPa, $V = 200$ °C/min; (3) few step SPS.

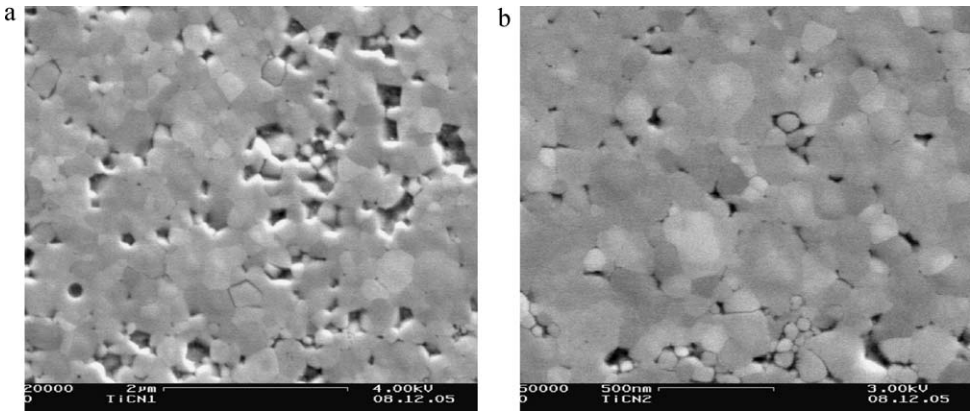

Fig. 5. SEM micrographs of nanostructured TiCN powder after SPS consolidation in vacuum: (a) one step SPS to 1600 °C, (b) few step SPS to 1400 °C.

dated materials than the single-stage regime (Fig. 2). However, under the multiple-stage regime, the TiCN nanopowder was consolidated up to 98–99% of relative density at only 1400 °C, while under the single-stage regimes, the maximum density of 94–96% was achieved at 1470–1520 °C. In the SPS process, the densification during the first stage of consolidation is preferably controlled by particles rearrangement, while the following stages are controlled mostly by diffusion. By increasing pressure and decreasing heating rate during the consolidation, it was possible to extend the particle rearrangement period from 800 °C up to about 1200 °C. This gave an advantage of maintaining higher densification rate keeping the grain growth minimal (curve 3, Fig. 4). On the final stage of the SPS process (above 1200 °C), the grain boundary and lattice diffusions dominate forming homogeneous porous and grain structure. An estimated average grain size of TiCN sintered under the single-stage regime was about 320 nm, while the multiple-stage regime resulted in twice smaller average grain size, about 150 nm (Fig. 5).

4.2. Properties of nano-TiCN

Mechanical properties of consolidated materials are the function of their final microstructure. The Vickers hardness and fracture toughness of TiCN bulk nanocomposites sintered under the multiple-stage regime was measured as 21.6 GPa and 3.2 MPa $m^{1/2}$ respectively, which is in a good agreement with data obtained for bulk TiCN materials by other investigators.[12] At the same time, TiCN sintered under the conventional single-stage regime up to 1600 °C demonstrated relatively high residual porosity and relatively low mechanical properties (see Table 2). Usually, to eliminate the residual porosity the isothermal hold at high temperatures is required. But in this case, the uncontrolled grain growth may take place leading to deterioration of mechanical properties.

To explore the advantage of fine grained microstructure for TiCN composites, the nanohardness tests were carried out. The loading–unloading curves obtained by a Berkovich diamond indenter at 10 and 20 cN load conditions are shown in Fig. 6. The elastic modulus of the material was also obtained during the nanohardness test. Values of 33 GPa for nanohardness and 378 GPa for elastic modulus were obtained. Some differences between nano- and Vickers hardness could be explained by the different amount of material involved in the tests. Nanohardness of TiCN is in a good agreement with data obtained for TiCN thin films.[13] During the nanoidentation, only the surface layer of material is tested, while the Vickers hardness tests (loads up to 10 kg) involves much larger area of the specimens.[14] It was not possible to obtain a reliable nanohard-

Table 2
Properties of SPS consolidated materials.

Material	TiCN	TiCN
SPS regime	Non-linear	70 MPa, 200 °C/min
Final temperature (T_f) (°C)	1400	1600
Relative density	0.98	0.94
Average grain size (nm)	150	320
Fracture toughness (k1c) (MPa $m^{1/2}$)	3.2	–
Vickers hardness (HV) (GPa)	21.6 ± 0.9	11.3 ± 2.4
Nanohardness (GPa)	33 ± 0.9	–
Elastic modulus (E) (GPa)	378	–

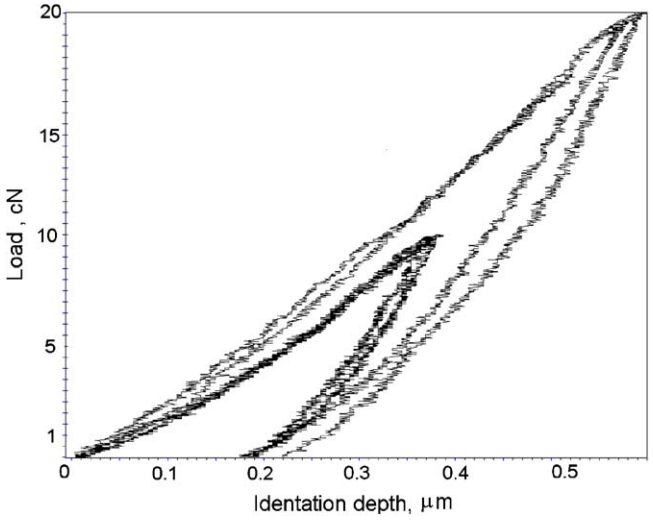

Fig. 6. Indentation curves for SPS consolidated TiCN.

ness data for TiCN samples sintered under the single-stage regime up to 1600 °C due to high residual porosity of the samples.

Additional investigations of the grain boundaries of the SPS consolidated materials are necessary to better understand the mechanism of hardening and to better predict the relationship between material's properties, microstructure and SPS consolidation regimes. Such multiple-stage SPS regimes utilizing RCS technology may also be applied for wide variety of materials in order to produce near fully dense ceramic composites with very fine microstructure.

5. Conclusions

Implementation of the multiple-stage regime for densification of nanocrystalline powders via spark plasma sintering was found to be promising for production of dense nanocrystalline materials at lower process temperatures. For example, 70 nm TiCN nanopowder can be successfully consolidated at 1400 °C into a near fully dense TiCN nanocomposite with average grain size about 150 nm. In comparison, using the traditional single-stage SPS regime, the same TiCN nanopowder can be consolidated only up to 94–96% of relative density at 1520 °C with average grain size about 320 nm. Nanohardness and fracture toughness of the TiCN nanocomposite consolidated under the multiple-stage SPS regime have been measured as 33 ± 0.9 GPa and 3.2 MPa $m^{1/2}$ respectively.

Acknowledgements

The authors wish to thank B. Weise for his kind help regarding the experiments, K. Sempf (FESEM), N. Dubovitskaya (TEM) and O. Butenko (Nanohardness) for their relevant technical support, and Dr. A. Polotai for fruitful discussion.

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