Synthesizing and Consolidation of Mechanically-Induced Solid-State Reacted $Ti_{50}C_{50}$ Nanopowders and Subsequent Consolidations

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ABSTRACT

High-energy ball mill for synthesizing of nanograined of $Ti_{50}C_{50}$ powders starting from elemental Ti and C powders. A single phase of NaCl-type TiC was obtained after 6 h of the ball milling time. The powders obtained after 200 h of the milling time possessed spherical-like morphology with average grain size of 10 nm, respectively. The end-product obtained after 200 h of the ball milling time, were then consolidated into full dense compacts, using spark plasma sintering at 1420 ^oC 1550 ^oC under 32.1 MPa, using heating rate of 500 ^oC/min, respectively. The Vickers hardness, Young's modulus, shear modulus and fracture toughness of as-spark plasma sintered samples were measured and found to be 32.1 GPa, 447 GPa 151 GPa and 6.4 $MPa.m^{1/2}$, respectively. The effect of consolidation approach on the grain size and mechanical properties have been investigated and discussed.

Keywords: Hard Materials, Ball Milling, Powder Consolidation, Nanomaterials, Nondestructive testing

1 INTRODUCTION

Carbides, especially those of the transition metals of groups IV and V in the periodic table, possess unusual properties that make them pioneering engineering materials for many industrial applications. The cubic form of TiC, which has NaCl structure, with its extremely high melting point (3100 ^oC) is a refractory material having some of the characteristic properties of metals (luster, metallic conductivity, etc.) [1].

In addition, it has extraordinary hardness, excellent resistance to wear and abrasion and infusibility. In the industrial scale of production, TiC is prepared at a very high temperature (1727 – 2100^oC) by direct reaction between metallic Ti and carbon or by reduction of TiO_2 under vacuum or inert gas, using graphite as reducing agent [2].

In the present study, and contrary to the industrial approach for preparing such important materials, we have succeeded to synthesize a single phase of $Ti_{50}C_{50}$ nanopowders, using high-energy ball milling technique. The ball milling procedure took place at ambient temperature in an argon gas atmosphere. The end-product that obtained after 200h of ball milling was consolidated into full dense nanocrystalline compacts, using spark plasma sintering (SPS) technique.

2 EXPERIMENTAL

The starting materials of pure elemental Ti metal (<45μm, 99.98 %) and carbon powders (<10 μm, 99.99 %) were balanced and well mixed in a glove box under a helium gas atmosphere (99.99%) to give the desired nominal composition of $Ti_{50}C_{50}$. The mixed powders were then sealed together with twenty five balls made of hardened Cr-steel into a hardened Cr-steel vial (220 ml in volume) under helium gas atmosphere, using gas-temperature-monitoring system (GST). The ball-to-powder weight ratio was 40:1.

The milling process was carried out at room temperature using high energy ball mill. The ball-milling experiments were interrupted after selected milling times and a small amount of the powder was taken from the vial in the glove box.

The synthesized nanopowders and their consolidated bulk materials obtained by consolidation process using SPS approach, were characterized by X-ray diffraction (XRD), high resolution transmission electron microscope/energy dispersive X-Ray spectrometer (HRTEM/EDS), field emission scanning electron microscope (FESEM) and electron probe micro analyzer electron microscope/EDS (EPMA/EDS).

The microhardness together with microfracture-toughness of the consolidated samples were investigated by Vickers hardness (VH) tester and nanoindenter, respectively. Nanoindention approach was employed to investigate the Young's modulus, stiffness modulus,

nanoscratch, viscoelastic creep behaviors and stress-strain curve. Moreover, The Young's modulus properties were determined via approach. In addition, the shear modulus, bulk modulus and elastic modulus were investigated by pulse-echo overlap ultrasonic technique.

3 RESULTS AND DISCUSSIONS

The XRD patterns of the ball milled powders are shown in Fig. 1(b) after selected milling time. Obviously shown, a single phase of TiC was obtained after 5 h of the ball milling time. Increasing the milling time (50-200 h) leads to a decrease in the grain size, indicated by the broadening in the Bragg peaks, as shown in Figs. 1(c) and 1(d). The lattice parameter of this end-product was calculated to be 0.433 nm in a good agreement with the reported value of NaCl-type TiC.

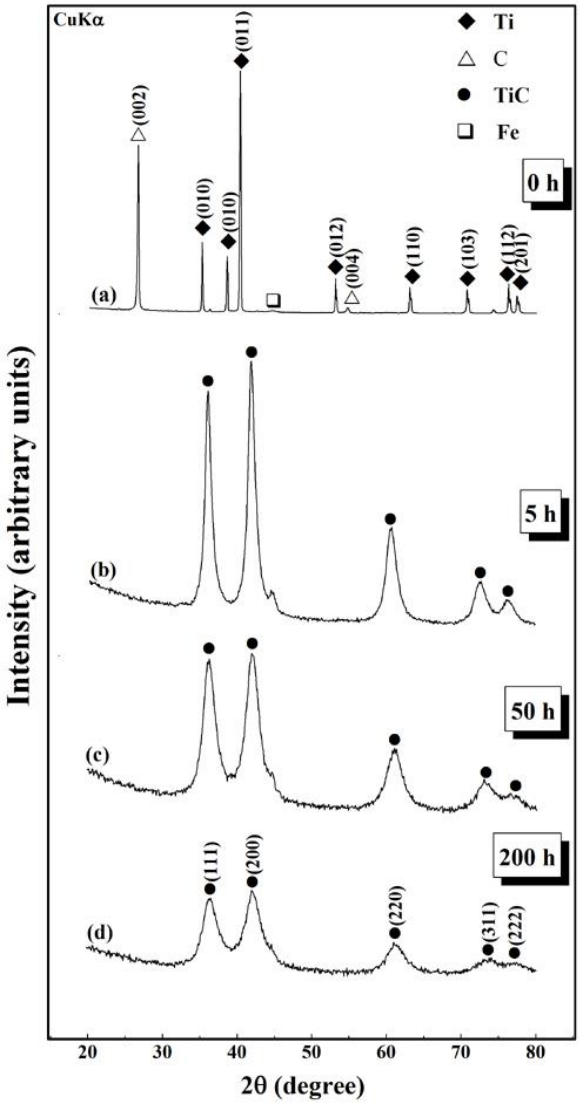

Figure 1. XRD patterns of the $Ti_{50}C_{50}$ powders after (a) 0h, (b) 5h, (c) 50h and (d) 200 h of the ball milling time.

The bright field image (BFI) and the corresponding selected area diffraction pattern (SADP) of the powders obtained after 5 h of the ball milling time are displayed in Figs. 2(a) and 2(b), respectively. The powders have large size grains size distributions ranging from 40 – 200 nm in diameter with of irregular shapes (Fig. 2(a)). No free Ti and/or C crystals could be observed after this stage of milling (Fig. 2(b)), as indicated by the Debye-Scherrer rings corresponding to NaCl-like TiC. The image of the scanning transmission electron microscopy (STEM) for the powders milled for 150 h (Fig. 2 (c)) indicates a dramatic decreasing in their grain sizes upon milling for 150 h to have grain size distribution in the range between 2 nm to 18 nm in diameter. Obviously shown, the powders obtained after this stage of milling enjoy homogeneous shapes spherical-like morphology (Fig. 2(c)). Moreover, the SADP of the powders obtained after 150 h still show clear fcc rings, as displayed in Fig. 2(d).

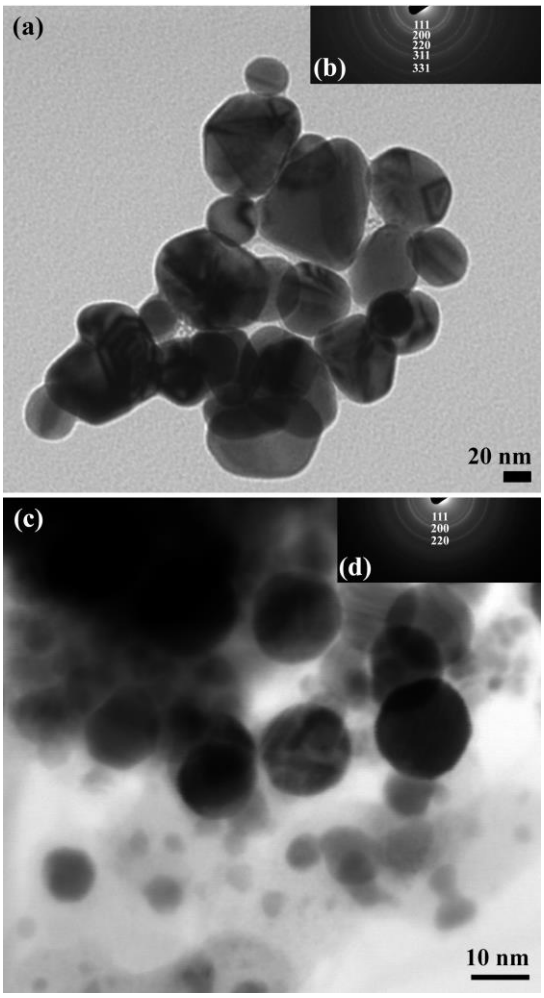

Figure 2. BFI and the corresponding SADP of the powders obtained after 5 h of the ball milling time are shown in (a) and (b), respectively. STEM and SADP of the powders that were ball milled for 150 h are presented in (c) and (d), respectively.

After 200 h of the ball milling time, the powders consist of nano-cells (less than 10 nm in diameter) with spherical-like morphology, as shown in Fig. 3.

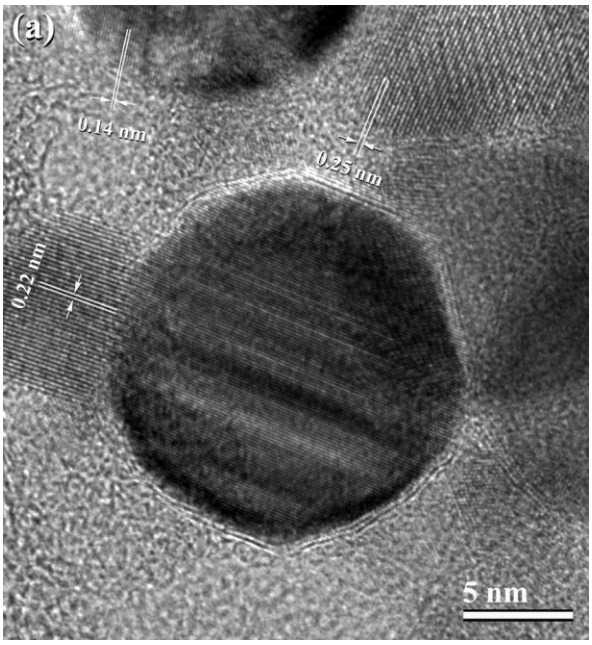

Figure 3. HRTEM micrograph of $Ti_{50}C_{50}$ powders after ball milling for 200h.

The high angle annular dark field (HAADF)/STEM for the sample obtained after 200 h of the ball milling time and the corresponding energy-dispersive x-ray spectroscopy (EDS) dot mapping of elemental Ti and C, are shown in Figs. 4(a), 4(b) and 4(c), respectively. Obviously, the intensity of the dots corresponding to particular Ti and C is proportional to their concentration at the particular locations. No segregations on a nanoscale scale of the elements can be detected and the elements are distributed homogeneously, indicating the formation of a homogeneous TiC material and the absence of any unprocessed Ti and/or C powders. The spot elemental analysis of the powders is closed with the starting nominal composition of equiatomic $Ti_{50}C_{50}$.

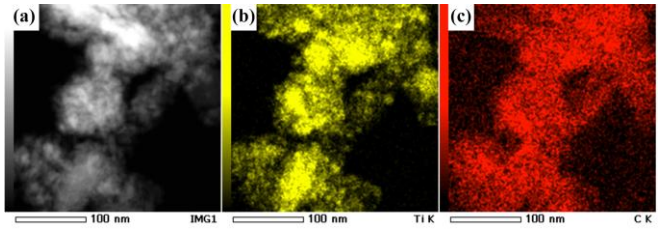

Fig. 4. (a). Image of the high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) for the sample obtained after 200 h of the ball milling time. The corresponding EDS dot mapping of elemental Ti and C are shown in Figs. 4(b) and 4(c), respectively.

Figure 5 shows the SEM micrographs of the powders obtained after 50 h (Fig. 5(a)) and 200 h of the ball milling (Fig. 5(b)).

After 50 h, the powders consist of agglomerated spherical clusters with an average particle size of about 500 nm in diameter (Fig. 5(a)). Increasing the ball milling time to 200 h leads to a significant particle refinement to obtain fine powder particles with an average size of 45 nm, as shown in Fig. 5(b). We should emphasis that the observed agglomeration of the nanopowder particles here is dominated by van der Waals, Coulomb forces and electrostatic forces [3].

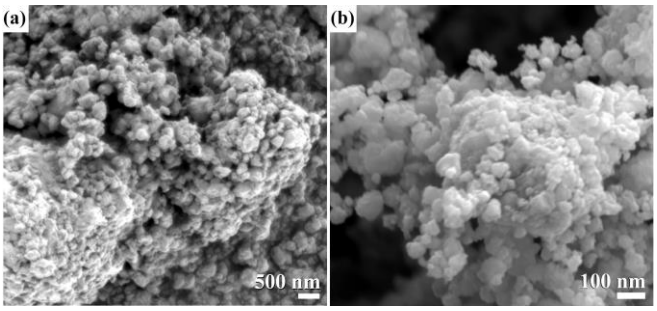

Figure 5. SEM micrographs of $Ti_{50}C_{50}$ powder particles obtained after milling for (a) 50 h and (b) 200 h of the ball milling time.

The bright field image (BFI) of the high-dense consolidated bulk materials obtained by SPS at 1420 ^{o}C and 1550 ^{o}C, are presented in Figs. 6(a) and 6(c), respectively together with their corresponding selected area diffraction patterns (SADPs). One can say that this consolidation step even at such rather high temperature does not lead to a sever grain growth and the size of the developed grains are ranging between 20-90 nm in diameter, as shown in Figs. 6(a) and 6(c).

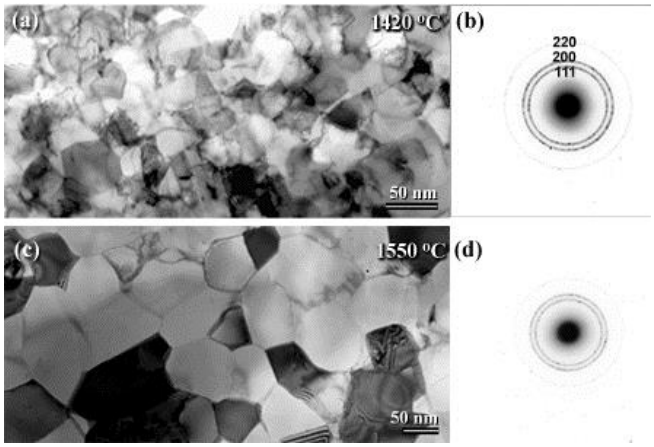

Figure 6. BFI and the corresponding SADPs of the samples obtained after 200 h of the ball milling time and then consolidated at temperatures of (a and b) 1420 ^{o}C and (c and d) 1550 ^{o}C.

It is worth to be mentioned here that the bulk materials obtained after sintering maintain their original crystal

structure of NaCl-TiC without any phase transformations, as shown in Figs. 6(b) and 6(d). The density of the consolidated sample at 1420 ^{o}C and 1550 ^{o}C were measured and found to be 5.19 and 5.21 g/cm^3 respectively, being nearly the theoretical density of pure TiC.

The measured VH of the samples consolidated at 1420 ^{o}C and 1550 ^{o}C are shown in Fig. 7 as a function of the ball milling time. Increasing the milling time leads to decrease the powder particle sizes that leads to significant increasing in the VH values. The VHs of the samples milled for 200h and then consolidated at 1420 ^{o}C and 1550 ^{o}C were measured and found to be 31.7 and 32.1 GPa, respectively. The average Young's modules investigated by pulse-echo overlap ultrasonic technique for the samples consolidated at 1420 ^{o}C and 1550 ^{o}C are 446 and 447 GPa, respectively.

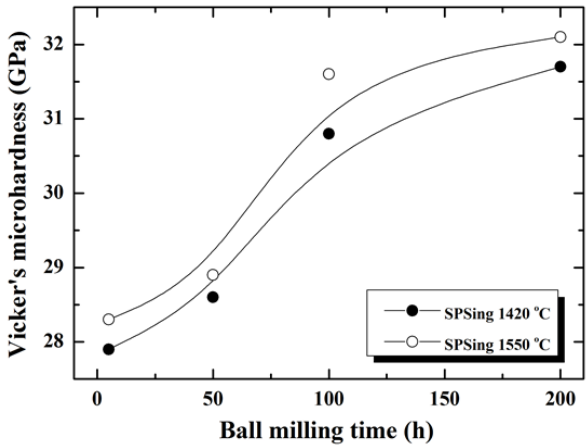

Figure 7. (a) Vicker's hardness and (b) Young's modulus of the consolidated samples after different ball milling time.

4 CONCLUSIONS

High-energy ball milling of equiatomic Ti and C powders under a helium gas atmosphere was utilized to synthesize of homogeneous nanograined TiC powders. The coarse grains (40 – 200 nm in diameter) of NaCl-type TiC obtained after 5 h of the ball milling time were significantly refined upon subjecting the powders to further ball milling (200 h).

The powders obtained after 200 h, which consist of fine grains (~ 10 nm) were consequently consolidated into full dense bulk samples, using spark plasma sintering.

The Vickers microhardness and elastic moduli (Young's and shear moduli) of the consolidated samples were measured as a function of the ball milling time. The effect of consolidation approach, ball milling time and grain size on the mechanical properties of TiC powders were investigated.

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