Effect of the Consolidation Techniques on the Mechanical Properties of Nanocrystalline $Ti_{55}C_{45}$ Powders Prepared by Mechanically Induced Self-Propagating Reaction

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ABSTRACT

Single phase of NaCl-type $Ti_{55}C_{45}$ nanorystalline powders were synthesized by ball milling of elemental Ti and C powders. The powders obtained after 200 h of the ball milling time possessed spherical-like morphology with average particle and grain sizes of 45 nm and 4.2 nm, respectively. The powders of the end-product were consolidated into full dense compacts, using hot pressing (HP) and spark plasma sintering (SPS) at 1500 ^oC and 34.5 MPa, using heating rates of 20 ^oC/min and 500 ^oC/min, respectively. Whereas HP of the powders led to severe grain growth (~436 nm in diameter), the as-SPSed powders maintained their nanograined characterizations (~28 nm in diameter). The effect of the consolidation technique on the mechanical properties will be presented discussed.

Keywords: Hard materials, ball milling, powder Consolidation, structure

1 INTRODUCTION

Advanced materials can be synthesized either by top-down [1] or bottom-up [2] approaches, using different available techniques. Since the first paper reported by El-Eskandarany in 1996 [3] on the possibility of synthesizing nanocrystalline TiC powders by high energy ball milling of elemental Ti and C powders under argon gas atmosphere at room temperature, many metal carbides and their nanocomposite systems have been prepared, using the same technique [4].

The worldwide interest on TiC material, in particular the TiC, nanophase is attributed to its unusual properties, which possesses a set of unique charcterizations and properties. These desirable properties always nominate this material for useful applications such as cutting tools and surface protective coating against severe erosion and corrosion. Consolidation of pure TiC nanograined powders into nanocrystalline bulk materials with grain sizes less than 100 nm carries out many challenges [6, 7].

The present work aims to study the effect of ball milling time and grain sizes on the microhardness, toughness and elastic moduli of hot pressed (HPed) and spark plasma sintered (SPSed) $Ti_{55}C_{45}$ materials synthesized by ball milling technique. The feasibility of using both each consolidation technique and their advantages/disadvantages on producing full-dense nanograined bulk materials are demonstrated and discussed.

2 EXPERIMENTAL PROCEDURE

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 $Ti_{55}C_{45}$. 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 ball-to-powder weight ratio as 40:1.

The milling process was carried out at room temperature using high energy ball mill at a rotation speed of 250 rpm. The ball milled powders obtained after 200 h of milling were consolidated in vacuum at 1500 ^oC under a pressure of 34.5 MPa, using SPS and HP techniques. The times needed for consolidation process to get full-density samples with relative density of above 99.5% (5.185 g/cm^3), using SPS and HP techniques were 10 and 800 minutes, respectively. The heating rates used for SPS and HP processes were 500 ^oC/min and 20 ^oC/min, respectively.

The average crystal structure of all samples was investigated by X-ray diffraction (XRD) with CuKα. The local structure of the synthesized material powders at the nanoscale was studied by 200 kV-field emission high resolution transmission electron microscopy/scanning transmission electron microscopy (HRTEM/STEM) equipped with energy-dispersive X-ray spectroscopy.

Vickers hardness test, with a load of 20 kg was employed to determine the hardness of the consolidated samples. In addition, Young's and shear moduli as well as Poisson's ratio of the consolidated samples were investigated at the room temperature by resonant frequency & damping Analyzing technique, using RFDA HTVP1600 equipment.

3 RESULTS AND DISCUSSIONS

The XRD patterns of mechanically ball milled Ti and C

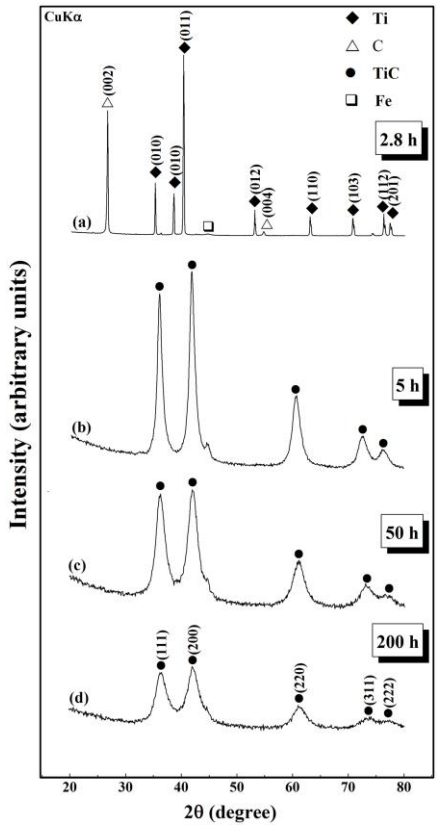

Figure 1: XRD patterns of $Ti_{55}C_{45}$ powders after (a) 2.8 h, (b) 5 h, (c) 50 h and (d) 200 h of high-energy ball milling time.

powders obtained after selected ball milling time are displayed in Fig. 1. After 2.8 h of the ball milling time (Fig. 1(a) the powders were polycrystalline mixture of Ti and C powders. The XRD pattern of the sample obtained after 5 h of the milling time is presented in Fig. 1(b). Obviously shown, all the Bragg-peaks corresponded to the starting reactant materials of Ti and C (Fig. 1(a)) are completely disappeared, whereas a single phase of TiC is appeared, characterized by sharp Bragg peaks of TiC (111), TiC (200), TiC (220), TiC (311) and TiC (222) reflections, as shown in Fig. 1(b). The lattice parameter (a_o) of the formed phase for TiC was calculated and found to be 0.433 nm, in a good agreement with the reported value (0.4327 nm). Moreover, the intensity ratio of these Bragg peaks are almost in a good agreement with those of the TiC powder, suggesting that the crystal structure of the obtained powders is NaCl-type. Remarkable broadening of the Bragg peaks of TiC powders obtained after 50 h of the ball milling time (Fig. 1(c)), suggesting a decreasing in the grain size of the powders after this stage of ball miling. Increasing the ball milling time to 200 h (Fig. 1(d)) leads to further increasing in the mechanical deformation that is generated by the milling tools, resulting further broadening of the Bragg peaks for TiC, associated with an increasing in the full width at half maximum (FWHN) values. This implies the formation of nanoscaled-TiC powders.

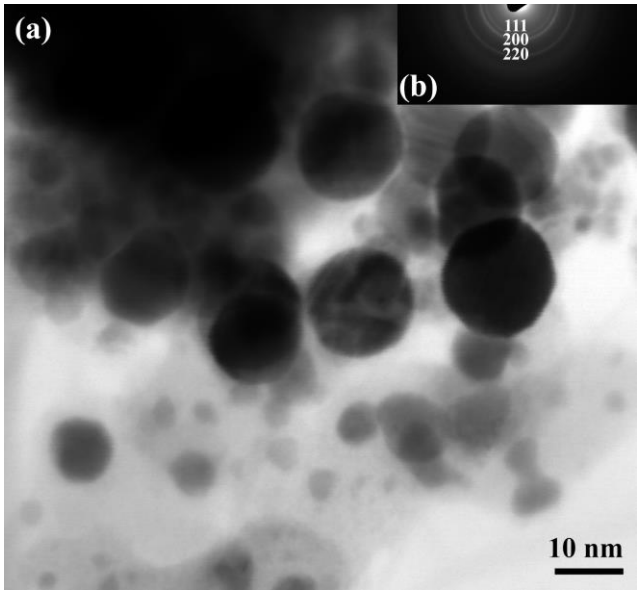

Figure 2: (a) STEM and (b) SADP of the powders obtained after 200 h of the ball milling time.

The image of the scanning transmission electron microscopy (STEM) for the powders milled for 150 h (Fig. 2(a)) indicates the formation of nanocrystalline powder particles having a 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(a)). Moreover, the selected area diffraction pattern (SADP) of the powders obtained after 150 h show clear fcc rings corresponding to NaCl-type TiC phase, as displayed in Fig. 2(b).

The HRTEM image of the powders obtained after 200 h of the ball milling time is shown in Fig. 3. The lattice fringe

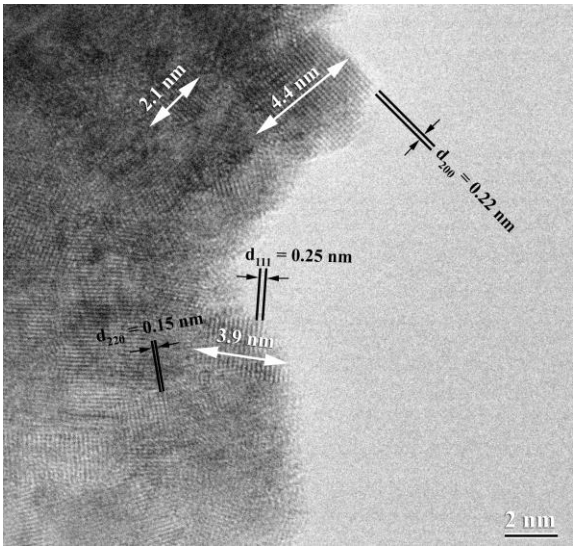

Figure 3: HRTEM image of the sample milled for 200 h of the ball milling time.

spacing of 0.15 nm, 0.22 nm and 0.25 nm indexed in the image match well with the interplanar spacing of TiC (220), (200) and (111), respectively. The average grain size calculated from the sizes of 47 grains (some of these grains are indexed in the figure) was 4.2 nm.

Figure 4 shows the BFIs of the cross-sectional view and the corresponding SADPs for the powders obtained after ball milling for 200 h and then consolidated by SPS (Figs. 4 (a), (b)) and HP (Figs. 4(c), (d)), respectively. Obviously, both consolidation approaches led to produce full-dense bulk materials, suggested by the existence of high-dense structure of equiaxed grains and the absence of any pores beyond the nanoscale, as displayed in Figs. 4(a) and 4(c). Moreover, it can be said that both consolidation approaches did not lead to any structural changes, implied by the Debye-Scherrer rings corresponding to NaCl-type TiC shown in Figs. 4(b) and 4(d). It worth to be mentioned here that the grains of as-SPSed $Ti_{55}C_{45}$ sample still maintain their nanocrystanilities with an average grain size of 28 nm in diameter, as displayed in Fig. 4(a). Contrary to this, the grains of the sample produced by HP under the same sintering conditions of same material were suffered from severe grain growth that led up to vanish their original nanocrystalline characterizations and to produce sub-microstructured grains with an average size of 436 nm, as shown in Fig. 4(c).

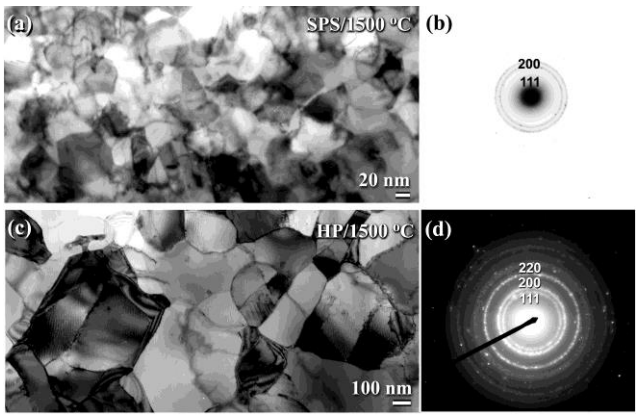

Figure 4: BFIs and the corresponding indexed SADPs of as-consolidated samples obtained by sintering the synthesized $Ti_{55}C_{45}$ powders, using (a, b) spark plasma sintering and (c, d) hot pressing techniques.

Figure 5 elucidates the dependence of the Vickers microhardness of as-SPSed and HPed $Ti_{55}C_{45}$ samples (Y1-axis) on the ball milling time (X-axis) and the grain sizes (Y2-axis). Based on the present results, increasing the ball milling time, which leads to decrease the powder and grain sizes of the ball milled powders, improves the microhardness characteristics of the consolidated samples, suggested by the monotonical increase in the values of Vickers microhardness, as shown in Fig. 5. One can conclude that increasing the ball milling time leads to decrease the grain size of the powders and this leads to a significant decrease in the grain size of the sintered samples. Thus, the grain sizes of the consolidated samples are depending on the original grain size of the as-milled powders used as feedstock materials for the consolidation procedure. Obviously presented, the powders obtained after 100 and 200 h of ball milling time and then consolidated by SPS have higher microhardness values (31.7 and 32.2, respectively) when compared with the same samples obtained upon powder hot pressing samples (21.6 and 22.2 GPa, respectively). The average grain sizes of $Ti_{55}C_{45}$ material obtained by SPS of 100 h and 200 h samples were 42 and 28 nm, respectively. In contrast to the SPSed samples, the grain sizes for the same materials obtained upon HP consolidation of 100 h and 200 h samples were 418 and 208 nm, as shown in Fig. 5. The dependence of the microhardness on the grain size is attributed to the grain boundary hardening effect due to Hall-Petch assumption. Moreover, it can be also concluded from the figure that optimizing of the ball milling time for preparing nanopowders particles should be combined with prober consolidation process in order to prevent dramatic grain growth of the consolidated materials that always lead to minimize their harness values.

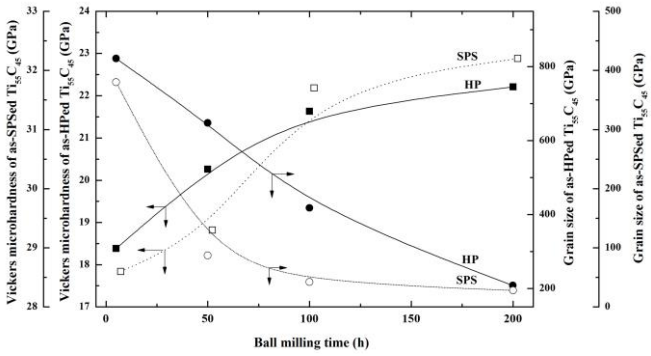

Figure 5: Effect of grain size and consolidation techniques on the Vickers microhardness of $Ti_{55}C_{45}$ sintered samples obtained by HP and SPS approaches.

The results obtained from at least 200-microhardness tests were used to design 3-D plot (Fig. 6). One can say that the microhardness values of SPSed sample, which are ranging between 31.70 – 32.35 GPa (Fig. 6), are very closed to each other, suggesting the homogeneity of the obtained bulk material and the absence of unreacted elemental powders.

The elastic moduli presented by Young's modulus (E) and shear modulus (G) of as-HPed (E^{HPed}, G^{HPed}) and -SPSed (E^{SPSed}, G^{SPSed}) samples are displayed as a function of the ball milling time and grain size in Figs. 7(a) and 7(b), respectively. The effect of grain size on the elastic moduli can be hardly seen for those samples obtained by HP approach (Fig. 7(a)). One can say that decreasing the grain sizes from 822 nm (5 h of ball milling) to 208 nm (200h of ball milling) had no pronounced influence on the E^{HPed}

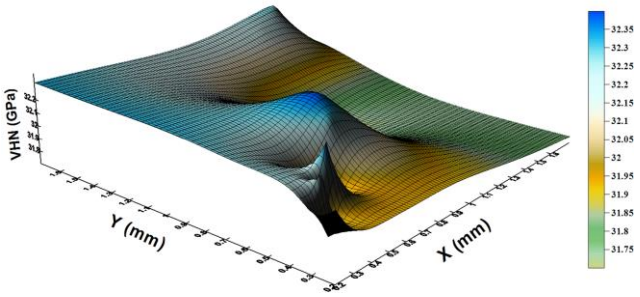

Figure 6: 3-dimensional plot presenting the variations in the microhardness values of the as-SPSed powders.

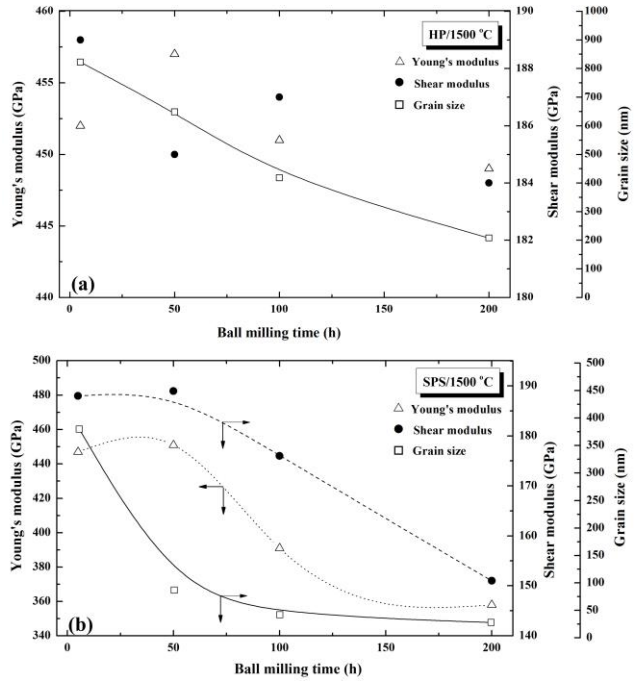

Figure 7: Dependence of Young's modulus shear modulus and grain size on the (a) HP and (b) SPS consolidation techniques.

that maintained a very closed values of 452 GPa and 449 GPa, respectively. In addition, G^{HPed} had near values of 189 GPa and 184 GPa for the 822 nm and 208 nm samples respectively, as shown in Fig. 7(a). When the grain sizes of as-SPSed samples were 380 nm (5 h of ball milling) and 87 nm (50 h of ball milling), no significant influence of the grain sizes could be detected on the values of E^{SPSed} and G^{SPSed}, as elucidated in Fig. 7(b).

In comparison with those samples produced upon HP of the ball milled powders, the E^{SPSed} of the samples obtained after 100 h 200 h of ball milling time and then consolidated by SPS were 391 GPa and 358 GPa, respectively, as shown in Fig. 7(b). Moreover, the G^{SPSed} of the same two samples were 175 GPa and 151 GPa respectively, being far below when compared with the HPed samples. It is worth to be mentioned here that the corresponding grain sizes of the samples of 100 h 200 h were 42 nm and 28 nm, as presented in Fig. 7(b). We can conclude that E and G of $Ti_{55}C_{45}$ bulk materials were not affected by decreasing of the grain size from 822 nm to 87 nm. An obvious effect could be only seen when the grain sizes were less than 87 nm.

4 CONCLUSIONS

High-energy ball milling of elemental Ti and C powders under a helium gas atmosphere was utilized to synthesize of homogeneous nanograined $Ti_{55}C_{45}$ powders. The gas-temperature-monitoring system, which was employed in the present study, shows that the reaction between the reactant material powders took place in a self-propagating reaction fashion. 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 (~ 4.2 nm) were consequently consolidated into full dense bulk samples, using hot pressing and 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 $Ti_{55}C_{45}$ powders were investigated.

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