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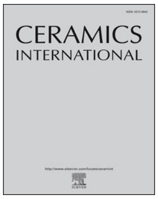

# Liquid phase assisted high pressure sintering of dense TiC nanoceramics

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## ABSTRACT

To address the difficulty of achieving high density while effectively suppressing grain growth in the fabricating of nanoceramics, this paper demonstrates a novel integrated approach, consisting of a solid-liquid reaction, high pressure and low temperature sintering, to prepare dense nanocrystalline TiC ceramics. Using Si as the additive, a low-viscosity Si liquid phase is formed under the sintering condition of 1200 °C/4.5 GPa. It is shown that both of the sintering aid and high pressure are crucial in achieving high density nanostructured TiC ceramics and controlling their microstructure and thus their mechanical properties. The pure TiC can be sintered to reach 95.3% of its theory density and, with the assistance of liquid Si additive, it can be sintered to full densification without grain growth by high pressure technique.

## 1. Introduction

Nanostructured ceramics often exhibit unique and exciting mechanical properties, such as improved strength, stiffness, wear resistance, fatigue resistance, ductility, and toughness [1–4]. However, bulk nanoceramics in dense forms are extremely difficult to fabricate. A lot of research and experiments have to be done to unveil their full properties.

Owing to its possessing excellent stability at high temperature, good oxidation resistance, high thermal conductivity, and good thermal shock resistance, TiC is considered as one of the most important ultra-high temperature ceramics (UHTCs) [5–7]. However, it is a challenging task to consolidate TiC due to its high melting point, strong covalent bonding, and low self-diffusion coefficient. The densification temperature of TiC normally exceeds 1700 °C, even when assisted by an external pressure [8,9]. Moreover, the finer of the starting powders, the more rapid grain growth ($d/d_0$) observed in the fabrication of bulk ceramics.

Abderrazak et al. synthesized nanostructured TiC by the spark plasma sintering (SPS) technique and the relative density of the bulk increased from 92.8% to 95.1% when the initial powder size decreased from 28 nm to 6 nm, but with grain growth increasing from 4.3 to 15.2 [10]. Cabrero et al. did the spark plasma sintering of nano-sized TiC powder (average particle size: 30–80 nm) at 1800 °C/75 MPa and observed ~ 95.4% densification [11]. Teber et al. optimized the SPS process and achieved a higher relative density of 97.9%, but it is accompanied by a larger grain growth ($d/d_0 = 30$) and the final grain size of the specimen close to 1 μm, beyond the definition of the nanoscale [12]. A dense nanostructured TiC material with a relative density of up to 99% was produced by a high-frequency induction heating sintering (HFIHS) process with simultaneous application of 80 MPa pressure and induced current (total power capacity is 15 kW) within 4 min [13]. In the process, the grain growth is restricted to 3.9.

It can therefore be concluded that the densification of the nanoceramics may lead to an inevitable grain growth, even by employing the novel sintering technique of SPS. To suppress the grain growth, an ultra-high isostatic pressure (> 1 GPa) can be applied to inhibit the diffusion and mass transport of the material across the grain boundaries, thus preventing the grain coarsening during the sintering. Meanwhile, a higher density can be achieved by the high pressure sintering process through a plastic deformation mechanism [14]. The ultra-high pressure was valid in suppressing the grain growth and further increasing the density in fabricating bulk nanostructured ceramics, such as $MgAl_2O_4$, SiC, and TiN [1,15,16].

Apart from the high pressure sintering, the liquid phase assisted sintering is another effective method of lowering the sintering temperature while at the same time enhancing the densification [17–19]. For example, Xue et al. developed a solid-liquid reactive sintering approach to prepare dense TiC at 1500 °C by hot pressing, in which the Ti-Si liquid phase reacted with TiC in-situ forming $Ti_3SiC_2$ platelets, and the $Ti_3SiC_2$ refined TiC grains and reinforced the obtained ceramics [19].

In this work, to deal with the issue of densification and grain

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growth, Si sintering aid is incorporated to TiC matrix and an ultra-high isostatic pressure (4.5 GPa) is employed. The Si melting point decreases from 1414 °C in ambient condition to around 1158 °C at 4.5 GPa [20]. In this way, a low-viscosity liquid phase can be formed in the sintering condition of 1200 °C/4.5 GPa, which is beneficial to the rearrangement and consolidation of TiC grains at relatively lower temperature by raising the coefficient of self-diffusion. In this study, both of the effects of the liquid additive and high pressure on the achieving high density TiC nanoceramics and controlling grain growth and thus their mechanical properties are investigated.

## 2. Experimental

### 2.1. Sintering procedure

Commercially available nano-sized TiC powder (purity > 98.5%, Cl < 1.0%, Cr < 0.1%, Si < 0.1%; average particle size: ~ 50 nm, Alfa Aesar) and silicon powder (-325 mesh, 99.999% metal basis, Alfa Aesar) were used as the starting materials in this work. The powders of TiC and Si (ration in wt%: 2, 5, 10, 15, 20) were mixed with ethanol in a ball-milling machine with tungsten carbide (WC) balls for 2 h milling. The slurry obtained was dried in a rotary evaporator to remove the ethanol. The dried powder mixture was then loaded into a mould and pressed into disc shape using a cold press method. After preforming, the as-prepared green body was put into a molybdenum (Mo) crucible and loaded into a large-volume cubic-type multi-anvil high-pressure apparatus (YL-800t, China), it was eventually multi-axially pressed from six WC anvils under ambient conditions. When the applied pressure reached 4.5 GPa, the densification was carried out at the sintering temperatures (1400 °C for pure TiC, and 1200 °C for TiC-Si mixtures). The heating rate was 150 K/min and the dwell time was 10 min. The cell temperature was applied by a cylindrical graphite cell and measured directly using a PtRh6%–PtRh30% thermocouple, and the pressure was estimated from the oil pressure reading calibrated by the bismuth phase transition under high pressure. Detailed experimental procedures can be consulted elsewhere [21,22].

### 2.2. Characterization

Relative densities of the sintered specimens were measured by the Archimedes method with deionized water as immersion medium. Crystalline phase identification was characterized by the X-ray diffractometry (XRD, X'pert Pro, PANalytical, Netherlands). Morphological and microstructural characterization of the ceramics were determined using the field emission scanning electron microscopy (FESEM, Zeiss Ultra 55, Germany) and transmission electron microscopy (TEM, Libra 200FE, Carl Zeiss SMT Pte Ltd). All the densified samples were polished with diamond slurry. Vickers hardness ($H_V$) and fracture toughness ($K_{IC}$) were measured by the depth sensing indentation method using diamond Vickers indentation at a load of 9.8 N and a dwell time of 10 s on the polished surface of the discs. $K_{IC}$ of the ceramics was obtained by the Vickers indentation according to the following equation [23,24]:

$$K_{IC} = 0.0028\left(H_V \frac{P}{L}\right)^{1/2} \tag{1}$$

where $H_V$ is the Vickers hardness, $P$ is the indentation loading force, and $L$ is the sum of the crack lengths.

## 3. Results and discussion

### 3.1. Microstructure

Fig. 1 shows the X-ray diffraction patterns taken from the TiC starting powders and also the ceramics sintered at 4.5 GPa and 1200 °C in 10 min. The XRD analysis confirms that the main peaks correspond to TiC (PDF No. 32-1383), and also that other phases such as SiC (PDF No. 29-1129) and $TiSi_2$ (PDF No. 35-0785) exist in the ceramics. The peaks have been indexed in the figure. As both TiC and SiC are cubic, the diffraction peaks of TiC and SiC are very close. The diffraction pattern collected from the TiC-5 wt% Si ceramic (red line in Fig. 1) shows some weak peaks corresponding to $TiSi_2$, and SiC is difficult to distinguish from the main peaks due to the limited content. When the Si additive increases to 20 wt%, not only $TiSi_2$, but also SiC can be observed in the pattern (blue line in Fig. 1). The results indicate that the reaction among these materials occurs as follows:

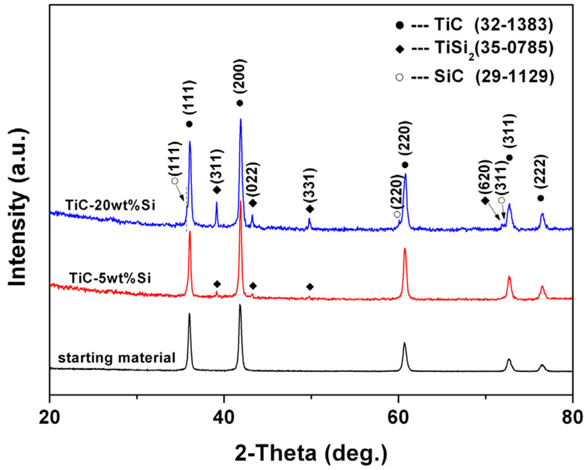

**Fig. 1.** X-ray diffraction patterns of the TiC starting material and the TiC based ceramics with 5 and 20 wt% Si additive, respectively.

$$TiC + 3Si \rightarrow SiC + TiSi_2 \tag{2}$$

Fig. 2 shows representative FESEM images of the starting powders and the fracture surfaces of the ceramics with different amounts of Si additive fabricated under the pressure of 4.5 GPa and soaking time of 10 min. The sintering temperature for pure TiC is set at 1400 °C, and it reduces to 1200 °C for the specimens with sintering aids. It can be seen that all the ceramics show nanocrystalline grains and dense microstructure. In comparison with the starting powders, grain size of the sintered samples keeps in the initial range because of the high pressure compression. On the fracture surfaces of the TiC based nanoceramics with Si additive (Fig. 2c-d), second phase centralized regions are characterized by darker contrast, as marked by the arrows in Fig. 2c. The second phases embed in the main phase and present less-particulate structure compared with the precursor counterparts (inset of Fig. 2d), which attributes to the formation of a low-viscosity liquid phase because Si has a melting point of ~ 1158 °C under 4.5 GPa. During sintering, the liquid Si filler distributes among the grains of the main TiC phase and reacts with it to form intergranular phases between them.

For further identification of the elements distribution in the ceramics, selected area EDS elemental mapping analysis was conducted. As can be seen clearly from Fig. 3, the ceramics is mainly composed of C (Fig. 3b) and Ti elements (Fig. 3c), while the Si element (Fig. 3d-f) distributes in the structure with a relatively concentrated shape. It suggests that the ceramics is mainly TiC, and other phases of Si based compounds disperse between them.

Fig. 4a presents TEM micrographs of the TiC-5 wt% Si ceramic and shows fully dense structure and nanoscale grains. The nanograins have an equiaxed shape with a size ranging from 15 to 80 nm, which is in perfect agreement with the value determined from SEM data (Table 1). No porosity is apparent in the investigated sample section. As shown by the selected area electron diffraction pattern (SAED) of the nanostructure (Fig. 4b), the main pattern corresponds to the cubic TiC phase, with weak orthorhombic $TiSi_2$ information. The crystalline structure