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# Densification kinetics and mechanical properties of tantalum carbide

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ABSTRACT

Sintering kinetics and densification of tantalum carbide (TaC) based ultra-high temperature ceramics (UHTC) processed using spark plasma sintering (SPS) were investigated. Samples sintered in the temperature ranging from 1600 °C to 2300 °C for 15 min under uniaxial pressure of 50 MPa showed increasing densification (~77% to 99% from 1600 °C to 2300 °C) accompanied by substantial grain growth (~0.57 μm to ~4.05 μm). Below 1900 °C, the densification mechanism was grain-boundary sliding with an apparent activation energy of 97.3 ± 10.2 kJ/mol. However above 1900 °C, the activation energy was found to be 232.7 ± 19.6 kJ/mol with grain boundary diffusion to be an active densification mechanism. The flexural strength (from 161.3 ± 10.4 MPa to 326.5 ± 10.5 MPa) and elastic modulus (from 375.7 ± 3.1 GPa 535.4 ± 4.7 GPa) was observed to increase with the increasing sintering temperature. The study explicitly establishes that the dense bulk TaC ceramic can be produced by SPS in a shorter time and lower sintering temperature, while maintaining the compositional stoichiometry.

## 1. Introduction

Ultra-high temperature ceramics (UHTC) are promising materials for applications in the aerospace and energy sectors [1–5]. Tantalum carbide (TaC) is a transition metal carbide which has the highest melting temperature (~3985 °C) among the UHTC family of materials [6]. Besides the high melting point, high elastic modulus (537 GPa), hardness (15–19 GPa), wear resistance, chemical inertness and moderate thermal expansion coefficient ($6.3 \times 10^{-6}\,K^{-1}$) make TaC an important candidate for ultra-high temperature usage like operating systems in rocket nozzles, cutting tools and some specific parts of space air-craft [7,8]. Consolidation of TaC has been performed using different techniques, e.g. pressureless sintering (PS), hot pressing (HP), hot isostatic processing (HIP), high-frequency induction heating, vacuum plasma spraying (VPS), spark plasma sintering (SPS) and dynamic consolidation [9–14]. Attaining a fair degree of consolidation entails high sintering temperature, as sintering typically occurs > 0.6 $T_m$, therefore, processing of pure TaC through conventional PS furnaces is difficult due to its high melting temperature, strong covalent bonding and low self-diffusion coefficient [15]. However, for monolithic TaC, pressure assisted sintering (HP [16,17] and SPS [18,19]) have typically been used to achieve full densification. The approach involving long time (HP, HIP etc.) appears to be inconvenient not only from the economical point of view, but also it often leads to coarsening of the microstructures and, consequently leads to poor mechanical properties. For instance, due to the long dwell time during HP of TaC ceramic at final temperatures (2000 °C, 10 °C/min), a significant grain growth with the final mean grain size of ~30 μm is observed [16].

In principle, the ability to produce a dense and highly resistant UHTC without the use of any secondary phases, would allow to exploit their potential up to the melting point. However, due to processing limitations, the addition of secondary phases such as Ni, Mo, Fe, HfC, NiC, $B_4C$, SiC, CNT, graphene etc. has been used to reduce the sintering temperature of TaC and attain full densification [7,15,18,20–25]. Another method of applying extreme pressure of 4.5 GPa (~150 times higher than conventional) during HP has also been assisted in enhancing the densification of TaC (up to 93%) at a lower sintering temperature (1200 °C) [26]. Also, TaC ceramic with a relative density of 96% has been successfully processed using SPS at 1400 °C [19].

The applicability of SPS to consolidate TaC powder over conventional HP in terms of densification and grain growth has been validated by *Khaleghi* et al. [18]. However, the investigation of sintering behavior (during HP of TaC) is limited to measuring the relative densities and densification rates with no elucidation of the densification mechanisms [16]. Indeed there are a variety of sintering techniques (PS, HP, VPS, SPS etc.) adopted for densification of TaC ceramic, but, the intrinsic sintering mechanism of stoichiometric TaC have not received any consideration. Recently, densification mechanism and kinetics have been investigated for the reactive hot pressed $ZrB_2$ ceramic in the temperature ranging from 1800 °C to 2100 °C [27]. The study has inspired (the present authors) to explore the potential of SPS in consolidating UHTC, like TaC. Hence for the first time, the intrinsic

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sintering mechanism, grain growth kinetics, and resulting microstructures of the SPS processed TaC-based UHTC has been studied in this work. It is important to be mentioned here that two different types of methods can be adopted for the evaluation of the activation energy, namely: *(i)* isothermal methods, e.g. rate controlled sintering method and *(ii)* non-isothermal methods, e.g. constant heating-rate method [28]. In the present study, authors have utilized the non-isothermal method to study the kinetics and densification mechanism (in terms of activation energy, $Q$ and grain boundary mobility) of TaC powder during SPS. SPS offers significant advantage for such investigations compared to conventional processing methods since it facilitates isothermal conditions in conductive powders such as TaC and allows an accurate in situ measurement of the shrinkage during densification. Nevertheless, this electric current assisted sintering (SPS) technology involves multi-field coupling of temperature, stress and electric field, which makes its densification mechanisms difficult to understand. It has been reported in literature that the activation energy is dependent on processing technique ($Q$ is low for the pressure and field assisted sintering when compared to conventional processing), initial grain size ($Q$ has lesser value for small initial grain size), pressure/stress ($Q$ decreases if the effective pressure is high), heating rates, current density ($Q$ decreases with increase in current density) [28–33]. Herein, no sintering aids/secondary phases were added in assisting the densification of TaC ceramic. Also, some evaluates have been made on the mechanical properties (flexural strength and elastic modulus) of the sintered TaC ceramic.

## 2. Materials and method

### 2.1. Processing of TaC ceramic

Commercial powder of TaC (Inframat Advanced Materials LLC, CT, USA, 99.7% pure, particle size < 2 μm) was processed via spark plasma sintering (SPS, Dr. Sinter Lab Series, SPS-515S, Japan) using 15 mm graphite die and punches with a heating rate of 100 °C/min. and temperature ranging from of 1600 °C to 2300 °C at a constant pressure of 50 MPa under a vacuum of < 6 Pa and holding time of 15 min. Prior to sintering, the morphology and structure of the TaC powder were analyzed using TEM (see Fig. 1). The ram displacement was observed throughout the SPS sintering to investigate the densification behavior. The final density values were measured using Archimedes principle (using ethanol as an immersion medium).

### 2.2. Characterization

Phase analysis of the SPS processed pellets was characterized using X-ray diffractometer (Bruker D8 Focus) with Cu $K_\alpha$ ($\lambda = 1.54$ Å) and scan speed of 0.5 s/step at step size of 0.02° in the range of 2θ from 20° to 80° with an operating current and voltage of 40 mA and 40 kV respectively. The C/Ta ratios of the commercial TaC powder and the SPS processed TaC ceramic were calculated using the Eq. (1) given by Storms [34], where $a_0$ is the lattice parameter of the TaC obtained from XRD pattern (using Xpert high score plus software).

$$C/Ta = -25.641 + 5.9757a_0 \quad (1)$$

Scanning electron microscopy (W-SEM, JSM-6010LA, JEOL, Germany) was performed to characterize fractured microstructures and grain sizes.

To evaluate the flexural strength of TaC ceramics, four rectangular flat bars with $l \sim 11$ mm, $b \sim 3$ mm and $d \sim 1.5$ mm as per ASTM C1161-13 standard [35] were cut from each sample using electrical discharge machining (EDM). Universal testing machine (UTM, Instron 1195) was utilized with a crosshead speed of 0.1 mm/min using 2 kN load cell for carrying out the four-point bending test (shown in Appendix Fig. A). Fracture strength is calculated using following formula:

$$\sigma_f = \frac{3PL}{4\,bd^2} \quad (2)$$

where, $\sigma_f$ is fracture strength, $P$ is maximum (breaking) load, $L$ is an outer span of the fixture, $b$ is breadth or width of the sample bar, and $d$ is the thickness of sample bar. For estimation of elastic modulus ($E$), Nielsen's formula [36] is utilized:

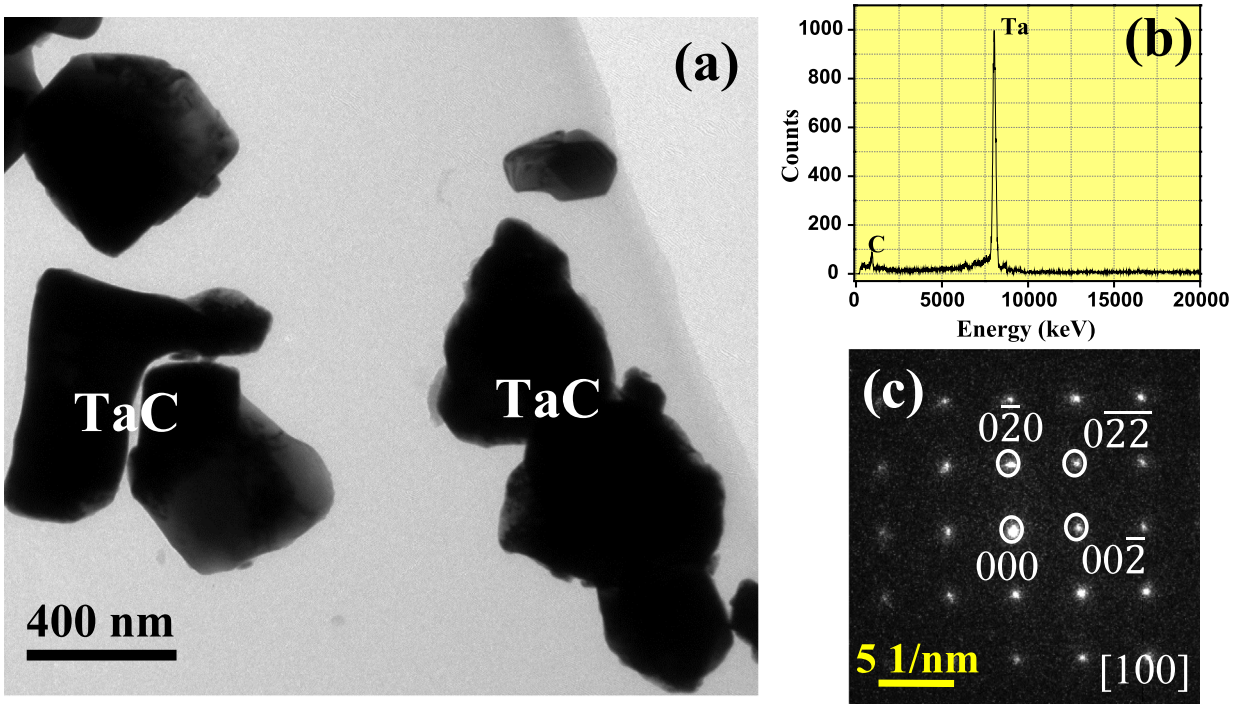


**Fig. 1.** (a) Commercial TaC powder prior to the onset of densification, corresponding (b) EDS spectrum showing presence of TaC, and (c) SAED pattern eliciting the cubic structure of TaC with zone axis of [100].