



Transient liquid phase sintering of tantalum carbide ceramics by using silicon as the sintering aid and its effects on microstructure and mechanical properties



Lianbing Zhong^a, Limeng Liu^{a,*}, Christian Worsch^b, Jesus Gonzalez^b, André Springer^b, Feng Ye^a

^a School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

^b Otto Schott Institute of Materials Research, Friedrich-Schiller-University Jena, Lobdergraben 32, D-07743 Jena, Germany

HIGHLIGHTS

- Tantalum carbide ceramics were densified by using 0.76–8.85 wt.% silicon as the sintering aids.
- The transient liquid phase sintering behavior of the material system was discussed.
- The elemental silicon improved densification and subsequently replaced by TaSi₂ and SiC.
- The tantalum carbide ceramic with 8.85 wt.% silicon addition showed a good flexural strength.

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ABSTRACT

Tantalum carbide composites with 0.76–8.85 wt.% elemental silicon as a sintering aid were fabricated by spark plasma sintering (SPS) at 1700 °C and 30 MPa for 5 min. The transient-liquid-phase sintering behavior, the microstructures and the mechanical properties of the tantalum carbide composites were investigated. Oxide impurities present on the surfaces of the tantalum carbide particles were eliminated by reactions with the elemental silicon in a temperature range from 1271 °C to 1503 °C to benefit densification. Then the silicon melted at its melting point temperature of 1413 °C to facilitate rearrangement of the tantalum carbide particles. By the end of the densification, the elemental silicon transformed into more refractory TaSi₂ and SiC in the consolidated ceramics by reactions with the tantalum carbide at temperatures lower than 1773 °C. Both TaSi₂ and SiC particles improved densification by physically pinning growth of the tantalum carbide grains. Further densification was resulted from creep flow of the silicides after brittle-to-ductile transformation of the silicides at temperatures <1650 °C. Due to the good effects of using elemental silicon as the sintering aid, all the compositions reached densities >96.7% theoretical. The average grain sizes in the consolidated materials decreased with the silicon addition from about 19 μm in the 0.76 wt.% Si composition to about 9 μm in the 8.85 wt.% Si composition. A good flexural strength up to ~709 MPa was reached in the 8.85 wt.% Si material due to full density and fine microstructure.

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1. Introduction

The IVB–VIB transition metal borides, carbides and nitrides are a family of compounds having a potential for applications in the next generation of hypersonic vehicles [1,2]. The high velocity flight or the re-entry conditions of the hypersonic vehicles require

slender aerodynamic shapes with sharp leading edges, thermal protection nose caps and air intakes which may operate in an oxidizing environment at temperatures over 2000 °C. For the cubic phase of the tantalum carbide compound (TaC), although limitations are imposed by the large density (JCPDS 35–0801: 14.498 g/cm³), the mild emissivity (0.40–0.46 between 2400° and 3500 °K) [3,4] and the inferior oxidation resistance relative to the zirconium diboride (JCPDS 65–7806: 6.102 g/cm³, emissivity about 0.7 at 1700 °K [5,6]), the application of the cubic tantalum carbide ceramics in the hypersonic vehicles is of lasting interest due to the

* Corresponding author.

E-mail address: liulimeng@hit.edu.cn (L. Liu).

high melting point (in excess of 3800 °C), good mechanical/chemical properties, such as high hardness, high elastic modulus, good resistance to chemical attack, and the good thermal (22.1 W/m K at 20 °C) [7]/electrical conductivities ($\rho = [102 + 0.0178 T (\text{°K})] \times 10^{-6}$ ohm cm, over the range 1400–3500 °K) [3] of the cubic tantalum carbide compound.

Generally, the monolithic tantalum carbide ceramic is extremely hard to densify because of the low self-diffusion coefficient of the compound, resulting from the strong covalent bond. Various methods have been tried to obtain fully dense tantalum carbide ceramics. A relative density of 97.5% was obtained for pure TaC [8] after sintering at 2300 °C for 0.5 h by using a fine TaC powder with a uniform distribution of particle size around $d_{50} = 250$ nm, relative to the 90.5% relative density when a TaC powder with a particle size of 15–25 μm was used [9]. Other approaches to enhance the densification of the tantalum carbide ceramics [8,10–12] were performed by increasing the mass diffusion beneficial to densification [13,14] while avoiding entrapment of residual pores inside the grains. Exaggerated growth of the TaC grains, which is in association with the oxide impurities present in the raw materials [15–19], always entraps the residual porosities, thus limits the final density a tantalum carbide ceramic can reach [10]. Pinning the growth of the grains was tried by Zhang et al. [20]. Addition of ~11 vol.% TaB₂ to a micron-sized tantalum carbide powder could result in >98% relative densities by hot pressing. SiC is also an effective additive in densifying the tantalum carbide ceramics. Addition of 5–40 vol.% α -SiC with a particle size $d_{50} = 1.0$ –1.2 μm could produce dense TaC–SiC composites with relative densities >98.6% after spark plasma sintering at 1600 °C [21].

Tantalum carbide powders mixed with a trace amount of transition metals (for example Fe, Mn, Ni, and Co [15,22–24]) or with some transition metal carbides (such as HfC and ZrC [25,26]) could also increase the densification of the tantalum carbide ceramics, probably due to increase in the densifying mass diffusion, though the transition metals may arise a liquid phase sintering [15]. The existence of a limited amount of metallic liquid was reasonable because of the presence of small metallic drops on the surfaces of the tantalum carbide ceramics containing metallic impurities after heating at 1600 °C [15]. In regard to the harmful oxide impurities usually present on the surfaces of the TaC particles, reducing agents such as C and B₄C [10] were used to reduce the oxides. The tantalum carbide composites with a 0.78 wt.% C addition reached a relative density of 97% by sintering at 2300 °C [10]. Sciti et al. [27] hot pressed tantalum carbide composites containing 15 vol.% TaSi₂ or MoSi₂ under a pressure of 30 MPa and reached a ~99% relative density at 1850 °C for 3 min and 1750 °C for 9 min for the 15 vol.% TaSi₂ and the 15 vol.% MoSi₂ composition, respectively. The enhanced densification was attributed to liquid formation [27,28], but also possibly due to creep flow of the silicides. Full densification may have been already reached in the tantalum carbide composites containing the TaSi₂ or MoSi₂ additives by hot pressing at a much lowered temperature of <1650 °C, merely due to the creep flow of the silicides after the brittle-to-ductile transitions of the silicide additives [29], needless to recall the liquid formation.

Other approaches to enhance the densification of the tantalum carbide ceramics [30–34] were in fact the various combinations of the previously mentioned techniques. For example, ultrafine tantalum carbide powders (40 nm) with 0.5–1% metallic impurities (Ni, Cr, Fe) could be densified at 1600 °C, after eliminating the oxygen impurities via prolonged reduction reaction by hydrogen [15]; Khaleghi et al. [33] used carbon nanotubes as an additive to the tantalum carbide ceramics and SPSed the powder mixtures at 2300 °C under 30 MPa for 20 min, to reach a 96% relative density; When sub-micron TaC, TaB₂ and carbon black mixtures were pressurelessly sintered at 2100 °C, high densities were obtained

[32]; Bakshi et al. obtained > 97% relative densities by mixing TaC with 1 wt.% B₄C (50 nm) [30]; Silvestroni et al. [34] hot pressed ultrafine tantalum carbide powders containing 5 vol.% MoSi₂ at 1900 °C, and thus reached a 95% relative density.

In addition to the successful methods stated above for the densification of the tantalum carbide ceramics, a transient liquid phase sintering (TLPS) approach may worth trying. In a typical TLPS process, the liquid which usually results from a proper sintering additive can be employed to promote densification, but the liquid should be subsequently eliminated by forming compounds of higher melting points, thus to avoid the possible bad effects of the additives on the mechanical properties at high temperatures of the final products. In this term, TLPS is obviously superior to the other processes for the densification of the ultra high-temperature ceramics for the reason that TLPS can reduce the deleterious secondary phases in the final products. Herein, fabrication of the tantalum carbide composites with 0.76–8.85 wt.% elemental silicon addition was tried by the SPS process. The use of the elemental silicon as the sintering aids showed the beneficial TLPS behavior in the investigated tantalum carbide material system. The reactive densification process, the formation of the microstructures and the mechanical properties of the consolidated tantalum carbide composites were investigated.

2. Experimental

Tantalum carbide (purity > 99%, with particle size $d_{50} \sim 1.0$ –1.5 μm ; Ningxia Orient Tantalum Industry Co., Ltd., Yinchuan City, China) and elemental silicon (purity > 99.99%, 1–3 μm ; Tianjin Fucheng Chemical Reagent Factory, Tianjin City, China) powders were used as the only raw materials. Batches of the powder mixtures, about 15 g each, with 0.76, 1.59, 3.51, and 8.85 wt.% Si (i.e. 5, 10, 20, and 40 mol.% Si), respectively, were mixed in plastic bottles containing SiC balls and hexane as the mixing media. After the slurries were dried and sieved, the powder mixtures were loaded into SPS dies for sintering.

The SPS equipment was a Dr. Sinter 1080 (Sumitomo Coal Mining Co. Ltd., Tokyo, Japan). The sintering process was performed at 1700 °C for 5 min under a 30 MPa uniaxial pressure. Before heating, the SPS chamber was evacuated to <6 Pa. At the first stage of heating, the temperature was automatically increased to 600 °C in 2 min, and the mechanical pressure increased from 5 to 30 MPa, simultaneously. Then a constant heating rate of 100 °C/min was used to reach the final temperature of 1700 °C. After holding for 5 min at 1700 °C, the SPS power was shut off to allow cooling and the mechanical pressure was reduced linearly from 30 MPa to 5 MPa in 1 min. The temperature decreased to ~860 °C by the end of the first 2 min.

The obtained samples (named after their starting compositions) were sectioned, ground and polished to 1 μm finish by using a diamond paste. Bulk densities were measured by the Archimedes method. Relative densities were calculated as percentage fractions of the measured bulk densities to the theoretical values determined by the law of mixtures. Deviations of the theoretical density values calculated by the law of mixtures from the true theoretical densities are expected, because the exact calculation of the true theoretical densities requires knowledge of the precise volume percentage and the bulk density of each phase present in the consolidated materials, neither is an easy task for the difficulty in determining the small concentrations of the secondary phases. Therefore, the major phases, namely TaC (JCPDS 35–0801: 14.498 g/cm³), TaSi₂ (JCPDS 65–3548: 9.140 g/cm³) and β -SiC (JCPDS 29–1129: 3.215 g/cm³) were counted for the calculation of the theoretical densities, because TaC, TaSi₂ and β -SiC are the only reaction products at completion of the reactions between the elemental Si and the TaC.

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