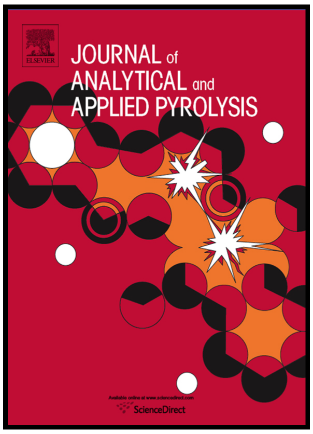

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Green Synthesis of Nanosized Tantalum Carbide (TaC) via Natural Polymer/Tantalum Oxide Hybrid Composites: A Sustainable Approach towards Enhanced Processing and Properties

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Abstract

This study provides a green method for producing nanosized tantalum carbide (TaC) by pyrolyzing natural polymer (Gum karaya)/tantalum oxide hybrid composites, which is both sustainable and environmentally benign. The carbothermal reduction, carried out at 1500 °C, produces cubic TaC with a cell constant of a_o=4.451 Å. The synthesised TaC reveals a near spherical morphology with an average size of 200 nm, far smaller than commercial TaC. The synthesised TaC displays a beginning oxidation temperature of 420 °C, as compared to the commercial powder (500 °C). Incorporating 5 wt% as-synthesized TaC to commercial TaC results in an impressive relative density of 98%, demonstrating the TaC ability as an excellent sintering aid. This green synthesis not only reduces the environmental impact of conventional methods, but also provides improved characteristics of nanosized TaC for advanced applications, contributing to the field of green nanotechnology by emphasizing safer production methods.

***Keywords*:** Tantalum carbide; Natural polymer; Hybrid composites; SPS; Sintering

1. Introduction

Tantalum carbide (TaC) emerges as a compelling material within the realm of advanced ceramics, boasting exceptional properties that render it integral to a myriad of cutting-edge applications. Recognized for its high hardness (15–19 GPa), melting point (3880 °C), Young's modulus (537 GPa), electrical conductivity (42.1 μΩ cm at 25 ºC), catalytic activity and good resistance to chemical attack

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and thermal shock [1–4]. The combination of both covalent and metallic bonds contribute to the characteristics [5] that makes it a candidate for applications in propulsion systems, rocket nozzles, leading edges of re-entry vehicles where the working temperature can be more than 3000 ^{o}C [1], cutting tools [6], as a hard coating on metal to increase corrosion and wear resistance [7], crucibles for molten materials and high temperature heating elements, TaC has become a cornerstone in the development of materials for extreme environments, such as aerospace and high-performance cutting tools [8].

The synthesis of tantalum carbide (TaC), heralded for its exceptional properties, has long been confronted by a spectrum of challenges that impact both the efficiency of production and the environmental implications of the process. TaC can be prepared via solid state synthesis by heating tantalum/tantalum oxide with carbon at a temperature above 1700 ^{o}C [9–11]. Other methods includes, self-propagating high temperature synthesis (SHS) [12], alternating-current discharge [13], high-frequency plasma [14] have been used to synthesize TaC. However, these processes are highly time and energy consuming because of the inefficient heat transmission between the induction coil and the reaction charge [9]. Although the liquid precursor route [15–17] has some advantages over the conventional route such as reduced processing time and power consumption and fine particle size product it has the demerit of creating toxic gases along with possible furnace corrosion due to the presence of chlorine in the inorganic salt used as the source of metal ions in the precursor [18]. However, these approaches pose significant challenges. High-temperature processes not only demand substantial energy consumption but also introduce environmental concerns due to the use of toxic precursors [19–21]. The demand for greener and more sustainable synthesis routes has, therefore, fueled exploration into alternative methodologies. In addition to environmental challenges, the conventional methods are associated with issues of size uniformity, scalability and reproducibility. The attainment of nanosized TaC particles with consistent properties becomes a formidable task, necessitating a paradigm shift towards innovative and sustainable synthesis approaches.

On the other hand, Densifying tantalum carbide (TaC) presents inherent challenges attributed to its robust covalent bonding, low self-diffusion coefficient, and notably high activation energy, recorded at 406 kJ/mol, surpassing that of all metals, oxides, and carbides [5]. The formidable task of achieving dense monolithic TaC has spurred investigations into various sintering-promoting methods. These include the use of ultrafine starting powders, application of high pressure, and incorporation of mixed carbides and metallic powders like boron carbide, hafnium carbide, niobium carbide, nickel, molybdenum, and iron. However, the addition of metallic powders or carbides as additives often results in increased grain growth, leading to compromised mechanical properties such as strength and toughness [22]. In recent efforts to overcome these challenges, attempts have been made to synthesize submicron TaC powder at lower temperatures, showcasing potential advantages in densification compared to coarser powders [23].

The inclusion of nanosized tantalum carbide represents a viable path to address densification difficulties of TaC, a material notoriously difficult to densify, yet ordinary sintering may drive rapid grain development (from 100 to 500 nm) [24]. Nanomaterials large surface area and reactivity make for faster sintering kinetics and more efficient nucleation during densification. Nanoparticles of TaC dispersed throughout the matrix have the potential to serve as efficient nucleation sites, fostering consistent grain formation while suppressing aberrant grain growth in the sintering process. Also, the enhanced densification efficiency may result from better particle packing made possible by the higher surface energy of nanoparticles. In addition, nanoscale TaC added during sintering can help lower the temperature of the process while simultaneously improving mass transport processes. The desired microstructure and mechanical characteristics are maintained while densification is enhanced.

So, in an attempt to synthesise TaC particles, we used a natural accessible green polymer (gum karaya) as the source of carbon and complexing agent and producing an organic-inorganic hybrid complex. This study takes into account the dynamic nature of TaC synthesis by presenting a sustainable method based on hybrid composites of natural polymers and tantalum oxide. High-temperature processes and environmental issues are common in traditional methods; therefore a more sustainable option is needed. In accordance with green chemistry principles, natural polymer/Ta-oxide composites can be a sustainable route towards the manufacture of nanosized TaC [25,26]. This research suggests a novel synthesis approach that not only attempts to improve TaC characteristics but also conforms to the goals of environmentally conscientious material manufacturing. The sustainable development of new materials requires the investigation of such green synthesis techniques. Characterization and behaviour comparison of the synthesised TaC powder with that of commercial TaC obtained by carbothermal reduction of tantalum oxide have been investigated. Synthesised TaC was compared to commercial TaC in terms of densification and microstructural development.

This research is new and original since it offers a bio-inspired and environmentally benign method for synthesising nanosized Tantalum Carbide by using natural polymer/Tantalum oxide hybrid composites. This technique deviates from the norm in that it makes use of cutting-edge, eco-friendly principles from the field of green chemistry. One unique strategy to enhancing TaC features and processing skills is to use natural polymers as a carbon source alongside reducing and binding agents. The use of bio-inspired materials in the synthesis underlines the originality of the study and aligns it with current efforts to create safer, more sustainable materials. This study shows how green chemistry and hybrid composites can be utilised together to generate fresh and inventive ways for the manufacturing of high-tech materials, and therefore provides a contribution to the burgeoning field of green material technology.

2. Experimental

2.1 Materials

Tantalum pentoxide (Ta_2O_5) with a purity of >99.9% was used in this study, as was gum karaya (GK) from Sigma-Aldrich (Dorset, UK). In addition, commercial tantalum carbide (TaC) powder was used as commercial reference material; this powder was purchased from H.C. Starck GmbH in Goslar, Germany and was used in its as-received form. These materials served as the backbone of the study's synthesis and characterization procedures, guaranteeing the quality and purity necessary for relevant results.

2.2 Preparation of gum karaya (GK)/ Ta_2O_5 hybrid composites

In the preparation of gum karaya (GK)/Ta_2O_5 hybrid composites, a meticulous procedure was followed to achieve optimal results. The process commenced with the dissolution of gum karaya in water at 60 °C, creating a stable solution. Subsequently, tantalum pentoxide was carefully added to the gum karaya solution, and the resulting mixture underwent refluxing at 60 °C for 2 hours. The composite material obtained was then subjected to a thorough drying process and subsequent grinding in an agate mortar to ensure a fine powder consistency. The prepared powder underwent a series of heat treatments in an alumina boat within a horizontal alumina tube furnace. This crucial thermal processing occurred at various temperatures ranging from 1000 to 1500 °C for a duration of 1 hour, all conducted under a controlled argon atmosphere with a flow rate of 60 mL/min. The entire heat treatment process adhered to a precise heating rate of 10 °C/min. This meticulous methodology was employed to synthesize gum karaya/Ta_2O_5 hybrid composites with varying properties, laying the foundation for further investigations into their structural and functional characteristics.

2.3 Spark plasma sintering

The synthesized TaC powder, obtained through pyrolysis of natural polymer/tantalum oxide hybrid composites, underwent spark plasma sintering (SPS) alongside commercial TaC powder (made by carbothermal reduction of metal oxide/carbon) to explore their densification behavior. Sintering was conducted in a vacuum at 2000 °C for 10 minutes using a load of 50 MPa. To assess the impact of the synthesized TaC powder on the densification of commercial TaC, the former was employed as an additive to the latter, constituting 2%, 5% and 10% of the mixture (5% gives the optimum result and represented and discussed in the result and discussion section). Cold pressing of 15g of the powder was carried out, placing it in graphite foil within a 20 mm diameter graphite die. The sintering process involved applying a constant load of 50 MPa from 1500 °C, maintaining it throughout the sintering and cooling phases. Heating and cooling rates were set at 100 and 50 °C min^{-1}, respectively. Shrinkage during sintering was monitored by recording the displacement of the sample along the pressing direction, while an optical pyrometer focused on the graphite die surface recorded temperature changes. The resulting time, temperature, force, and displacement profiles were detailed in Fig. 1. The sintered samples densities were subsequently measured using the Archimedes method in accordance with ASTM C373-14A standards [27]. This comprehensive approach provided insights into the sintering behavior and densification characteristics of the synthesized and commercial TaC powders.

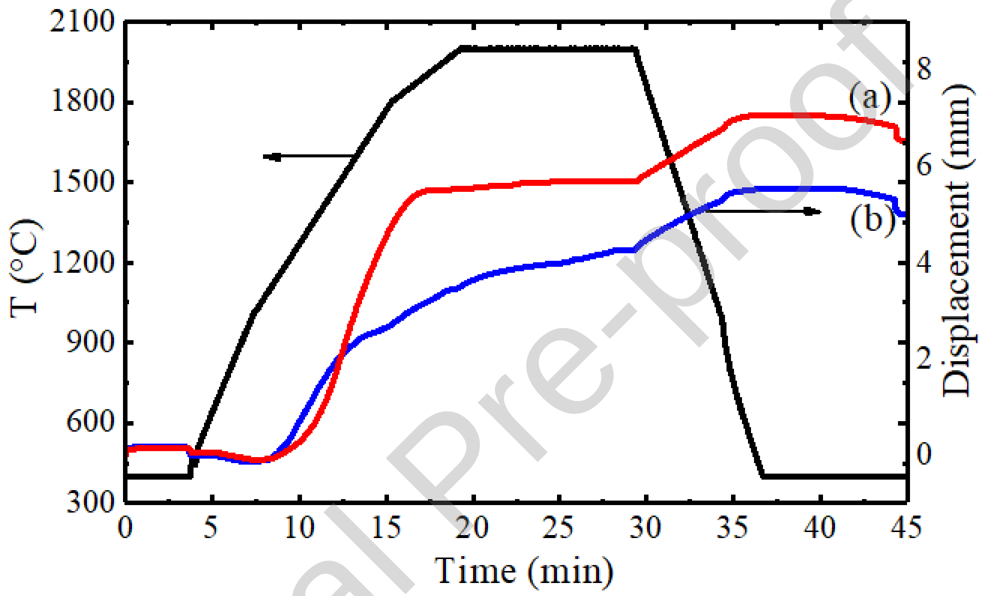

Fig. 1. SPS profiles of (a) commercial TaC, and (b) commercial TaC+5% as-synthesized TaC as sintering additive.

The phase composition of both the synthesized and commercial powders was investigated through X-ray diffraction (XRD) analysis, conducted using a PANAlytical Xpert3 diffractometer (Cambridge, UK). Cu Kα1 radiation with a wavelength (λ) of 1.540598 Å and a secondary monochromator were employed for this analysis within the 2θ range of 20° to 80°. The XRD peaks were indexed using Joint Committee on Powder Diffraction Standards (JCPDS) data cards #65-8145. Crystallite size was determined using the Scherrer equation, extracting valuable information about the structural characteristics and composition of the synthesized and commercial powders. This comprehensive XRD characterization provided insights into the crystalline phases present and their respective properties, contributing to the overall understanding of the materials under investigation.

Scanning electron microscopy (SEM) was used to extensively analyse the morphology of composite powders and sintered samples. Secondary electron imaging was undertaken using a scanning electron microscope (JEOL JSM 6010 LA, Tokyo, Japan) to explore fractography, providing insights into the surface and fracture features of the materials. Backscattered electron microscopy, which provides contrast according to grain orientation, was also carried out with the use of a Carl Zeiss AURIGA cross-beam (FIB-SEM) workstation (Oberkochen, Germany). This cutting-edge imaging method was used to investigate the microstructure and spatial distribution of the phases contained in the composite powders and sintered samples.

The structural alterations and interactions of organic ligands with metallic oxides in the as-prepared hybrid composites were elucidated through Fourier transform infrared (FTIR) spectroscopy. The FTIR analysis was conducted in the range of 4000-400 cm^{-1} using a Nicolet iS10 spectrometer (Thermo Scientific Company Ltd., Waltham, USA). This spectroscopic technique provided valuable insights into the chemical composition and bonding configurations of the hybrid materials. To enhance the accuracy of the analysis, baseline correction and peak-to-peak normalization were applied to all FTIR spectra, ensuring a reliable and comprehensive characterization of the hybrid composites.

The thermal behaviour of the as-synthesized hybrid composite was examined by thermogravimetry-differential thermal analysis (TG-DTA) NETZSCH STA 449 F1 (Selb, Germany) equipment was used for the thermal analysis. The analysis was conducted using a flow rate of 60 ml/min of argon while the samples were heated at a rate of 10 °C/min from 30 °C to 1550 °C. This technique offered vital information regarding the breakdown and carbothermic reaction profiles of the hybrid composite. In addition, TG-DTA analysis was performed in air for both the synthesised and commercial TaC powders, providing insight into their thermal behaviours in oxidative atmospheric conditions.

The experimental procedure followed the guidelines outlined in ASTM C373-14a standard method for determining the density of sintered TaC using the Archimedes method with distilled water as the immersion medium.

3. Results analysis and discussion

The XRD analysis of the tantalum carbide (TaC) powder synthesized through the described procedure reveals crucial insights into the phase evolution and crystalline structure at varying heat treatment temperatures as shown in fig. 2(a). The as-synthesized samples were subjected to XRD following heat treatment in a tube furnace at temperatures ranging from 1000 to 1500 °C for 1 hour. The XRD patterns obtained from the synthesized TaC powder revealed distinct diffraction peaks corresponding to different crystallographic planes. At temperatures around 1100 °C, the XRD patterns exhibited the coexistence of tantalum oxide and tantalum carbide phases, indicating the initiation of the carbothermal reduction process. As the heat treatment temperature increased, the intensity and sharpness of the peaks corresponding to tantalum carbide gradually strengthened, while those associated with tantalum oxide diminished. Notably, at 1500 °C, the XRD pattern displayed distinct peaks characteristic of pure cubic tantalum carbide, devoid of any traces of tantalum oxide or other contaminants. The emergence of strong and well-defined peaks at specific angles, such as 2θ = 35.9°, 42.6°, and 61.2°, corresponds to the crystalline planes of cubic TaC (111), (200), and (220), respectively. This observation underscores the efficiency of the carbothermal reduction process, achieving complete conversion to the desired TaC phase at elevated temperatures. The XRD analysis corroborates the phase transformation from tantalum oxide to tantalum carbide, signifying the efficiency of the carbothermal reduction process. The narrowing and intensification of the TaC peaks with increasing temperature suggest enhanced crystallinity and particle growth.

To further analyze the lattice parameter of the synthesized TaC, the Nelson-Riley function was employed, fitting the lattices determined from the principal peaks as shown in gig. 2(b). The resulting lattice parameter (a_o=4.451 Å) obtained from the XRD data aligns well with values reported in the literature (JCPDS No. 65-8145), confirming the successful synthesis of tantalum carbide with a cubic crystal structure. The absence of tantalum oxides and contaminants after heat treatment at 1500 °C validates the purity of the synthesized TaC, positioning it as a viable material for various applications requiring high-performance properties.

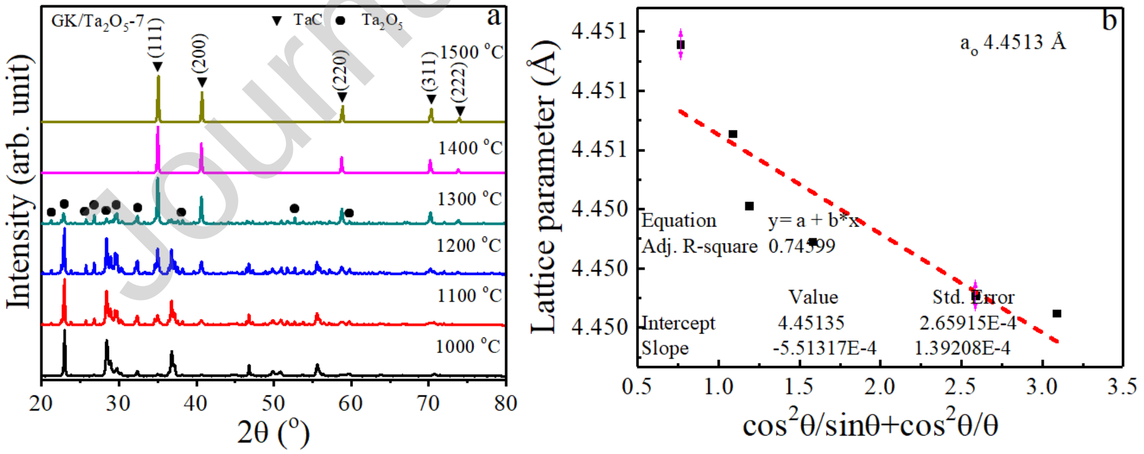

Fig 2(a). XRD of synthesized TaC powder heat treated 1 h at 1000, 1100, 1200, 1300, 1400 and 1500 °C under Ar, (b) estimation of lattice parameter by Nelson-Riley function for the sample heat treated at 1500 °C.

FT–IR spectroscopy has been used by numerous researchers [28–32] to get insight into structural alterations in materials. In order to detect structural changes and interactions of organic ligands with the tantalum oxide, the FT–IR absorption spectral band (Figure 3) of the hybrid's original components, including GK, Ta_2O_5, and the GK/Ta_2O_5 hybrid, was measured after drying at 110 °C. The O–H stretching band of the hydroxyl group is at 3330 cm^{-1}; the C=O stretching vibration is at 1725 cm^{-1}; the C=C band of CO^{2}–asymmetric stretching from carboxylic acid salts is at 1595 cm^{-1}; the CO^{2}–symmetric stretching is at 1417 cm^{-1}; and the C–H deformation is at 1371 cm^{-1}. The 1244 cm^{-1} band can be attributed to either CO^{2-}symmetrical or C–O–C asymmetrical stretching in carboxylic acid salts. Absorptive characteristics in the spectra of both Ta_2O_5/GK and pure Ta_2O_5 at 800–900 cm^{-1} are indicative of tantalum–oxygen bonding (Ta–O–Ta and Ta–O stretching vibrational band). The existence of a peak at 1171 cm^{-1}, attributed to C–O stretching in the Ta–O–C chain, and a vibration at 821 cm^{-1}, corresponding to the Ta–O stretching band in the Ta–O–C chain, demonstrates that Ta–O successfully constructed a bridge with GK via ion chelation [16]. During curing, the GK begins to dehydrogenate, as seen by the widening and weakening of the O–H stretching band in the hybrid precursor. There is a clear indication that the O–H is predominantly associated to the tantalum oxide in the FT–IR spectrum of the tantalum–based hybrid composite, as its intensity is lower than that of the O–H band in GK. After being subjected to carbonization and dehydration, the hybrid precursor's peaks broadened and lost intensity.

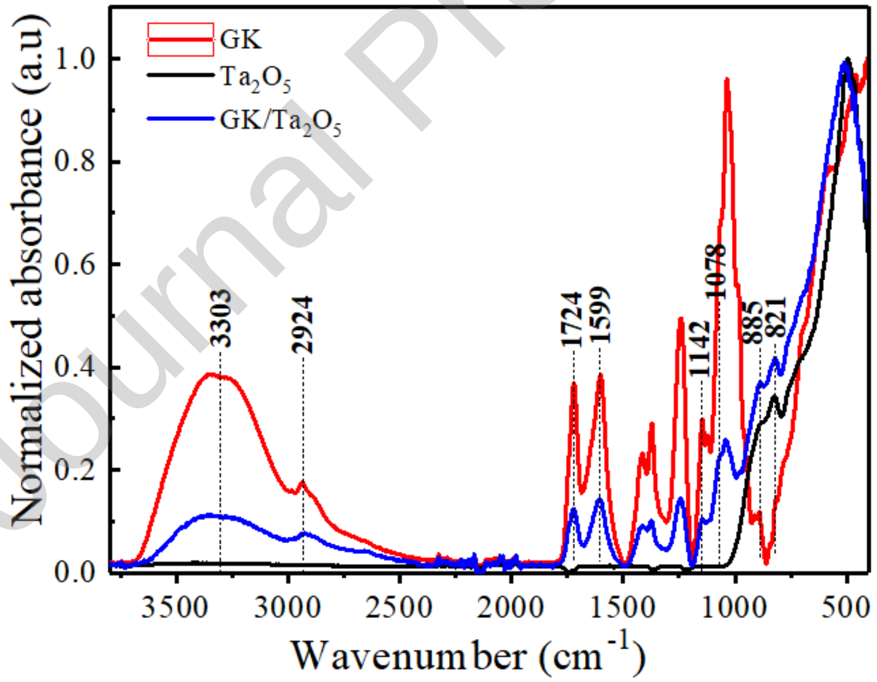

Fig 3. FT–IR of GK, Ta_2O_5 and as–synthesized GK/Ta_2O_5 hybrid composite dried at 110 °C.

From 30 to 1550 °C in argon, Fig. 4 displays the TG-DTG curves of the GK/Ta_2O_5 hybrid composite precursor. Initiating mass loss of 5% at 200 °C is attributed to the evaporation of adsorbed moisture. From the DTG curve, we can infer that mass loss is greatest at T1/125 °C. At T2/200 °C, the biopolymer chains began to decompose, resulting in a 30% loss of mass. DTG makes the gradual decrease in mass that occurs between 450 and 680 °C more apparent. From 800 to 1100 °C, almost no mass is lost. Evaporation of carbon monoxide during carbothermal reduction to generate tantalum carbide began causing a net loss of mass at around 1130 °C. Using the DTG curve, we can see that the highest rate of mass loss occurs at T3/1400 °C during the carbothermal reduction. The endothermic dip at 130 °C, the typical peak of evaporation of absorbed moisture or water, may be seen in the DTA curve. An exothermic peak at about 300 °C indicates that an organic polymer chain is being broken down into carbon. Crystallization of Ta_2O_5 does not exhibit any peaks because of steric hindrance from the organic group and also because the Ta_2O_5 is bound in a carbon matrix [33]. The thermal events observed in TGA, DTG, and DTA collectively reveal the complex decomposition, carbothermal reduction, and synthesis processes involved in the conversion of the GK/Ta2O5 hybrid composite precursor into tantalum carbide. The observed temperature ranges and peaks provide insights into the different stages of the synthesis and the corresponding reactions occurring within the material.

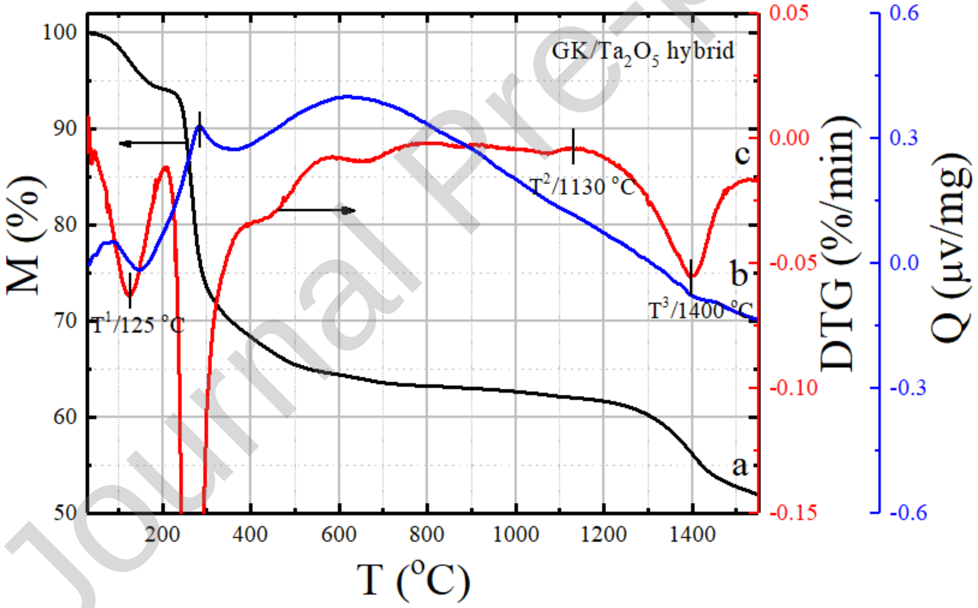

Fig 4. TG (a), DTA (b) and (c) DTG of as–synthesized hybrid composites precursor in argon where M denotes the mass of the sample, DTG is the first order derivative of the mass loss curve in order to understand the rate of mass loss with respect to time and Q represents the DTA heat flow where ΔT signal is measured in microvolts (µV).

The proposed reaction mechanism for the co-reduction-carbonization synthesis of tantalum carbide (TaC) from tantalum pentoxide (Ta_2O_5) and gum karaya (GK) is as follows:

1. Formation of Tantalum Oxide-Gum Karaya Complex

$$\mathbf{Ta_2O_5 + GK_{(s)} \longrightarrow Ta_2(O{-}GK)_{5(s)}}$$

Gum karaya reacts with tantalum pentoxide to form a complex, which acts as a precursor for composites.

2. Decomposition of Tantalum Oxide-Gum Karaya Complex:

$$\mathbf{Ta_2(O{-}GK)_{5(s)} \longrightarrow Ta_2O_{5(s)} + C_{(s)} + Volatiles_{(g)}}$$

The complex undergoes pyrolysis at high temperatures, producing tantalum pentoxide, carbon (C), and volatiles.

3. Carbothermal Reduction of Tantalum Oxide:

$$\mathbf{Ta_2O_{5(s)} + 7C_{(s)} \longrightarrow 2TaC_{(s)} + 5CO_{(g)}}$$

The formed carbon (C) reacts with tantalum pentoxide in a carbothermal reduction process, yielding tantalum carbide (TaC) and carbon monoxide (CO).

The proposed mechanism involves the initial formation of a tantalum oxide-gum karaya complex, followed by its pyrolysis to generate carbon. The carbon, in turn, undergoes carbothermal reduction with tantalum pentoxide, resulting in the formation of tantalum carbide. This mechanism is consistent with the experimental results obtained from XRD, FTIR, and TGA analyses, providing insights into the steps involved in the co-reduction-carbonization synthesis of nanosized tantalum carbide [34]. The Gibbs free energy (ΔG^o) calculations support the spontaneous and favorable nature of the reaction, especially at temperatures above 1135 °C [34].

Oxidation of transition metal carbide powders allows for the measurement of particle size, free carbon content, and grain size homogeneity [35–38]. As can be seen in Fig. 5, oxidation was studied in TGA in air on as-synthesized TaC powder and commercial TaC powder. Neither the as-synthesized nor the as-received commercial powder exhibits any mass loss up to 400 ^{o}C, as seen in the TG curve, demonstrating the absence of adsorbed moisture. As-synthesized and commercial TaC powders gain mass at 410 and 520 °C, respectively, indicating that the TaC is oxidised to form Ta_2O_5 and CO_2 [39]. The greater reactivity of the nano sized TaC particles causes faster oxidation, which accounts for the low beginning of oxidation for the as-synthesized powder. As the temperature is raised, more Ta_2O_5 is produced, indicating a quicker oxidation rate for the sample. When oxidised to Ta_2O_5, the mass increase was 10.7 wt% for as-synthesized TaC powder and 14.6% for commercial TaC powder. A theoretical mass gain of 14.5 wt% should be observed upon complete oxidation of TaC to Ta_2O_5. Because of free carbon from the pyrolysis of the organic polymer utilised in the complex or because the as-synthesized powder was non-stoichiometric, the maximum oxidation rate for the TaC powder we synthesised is lower [40]. It's possible that free carbon isn't a negative because it can aid in densification [34]. In such instances, it is possible to generate purer phases with smaller particle size (~30 nm) by producing precursors with greater C/Ta_2O_5 ratios. Excess carbon significantly limits particle development by decreasing the residual oxygen concentration in the final product because of the formation of a solid solution between TaC and C. Figure 5 displays the DTA curve, and the dotted line at 500 ^oC illustrates that the exothermic peak occurs due to the oxidation of the Ta component of TaC, which then leads in the synthesis of carbon and Ta_2O_5. The mass loss associated with the exothermic peak at 600 ^oC can be traced back to CO_2 evolution via free carbon oxidation. The TG curve flattens out after 900 ^oC, suggesting a mass increase of 10.7 and 14.6%, indicating that the oxidation process has been finished.

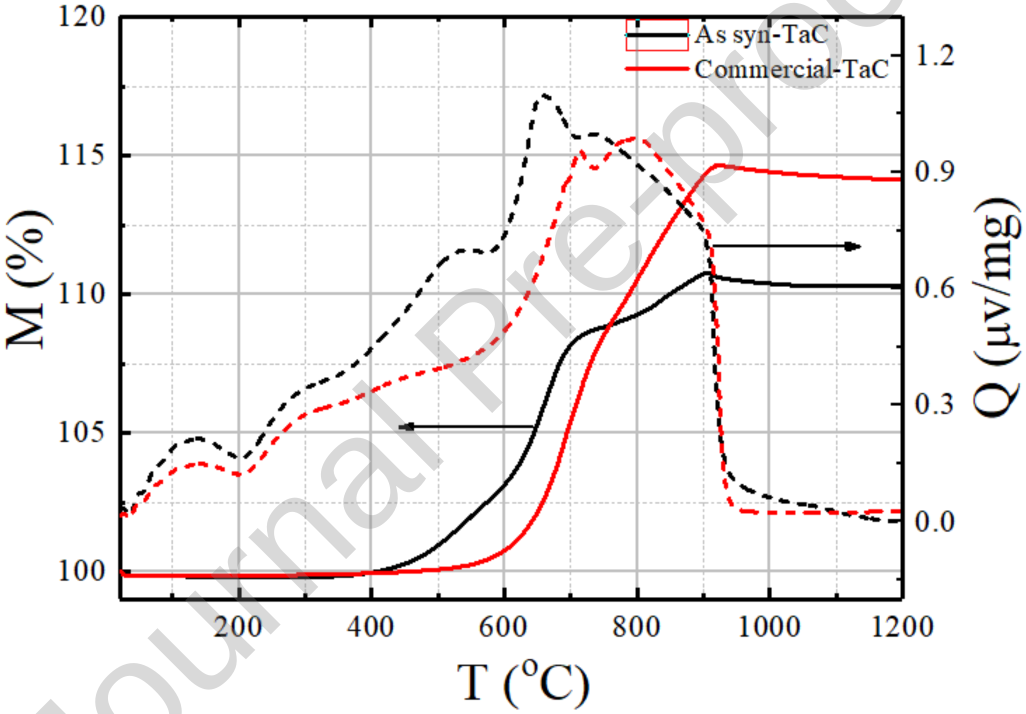

Figure 5. Thermogravimetric (TG) and differential thermal analysis (DTA) (dotted line) of commercial and as-synthesized TaC powder in air. (M is the percentage of mass and Q is the DTA heat flow; the T signal is expressed in microvolts (µV).

The field emission scanning electron microscopy (SEM) analysis provided valuable insights into the microscopical morphology of the TaC powder synthesised from gum karaya/tantalum pentoxide hybrid composites via carbothermal reduction, allowing for a comparison with the commercially available TaC particles from HC Stark Company. The synthesised sample shown in Fig. 6a has particles with an average diameter of 200 nm, as seen in the SEM image. Round and uniformly shaped particles like this are evidence that the carbothermal reduction method employing gum karaya/tantalum pentoxide hybrid composites is efficient. A regulated synthesis approach may enhance attributes and applications due to the nanometric size and homogeneous morphology. Figure

6b shows the microscopic morphology of the TaC powder that is now on the market. While the synthesised sample aggregated into smaller, softer particles, the commercial powder tended to form bigger agglomerates with a diameter of around 5 µm [9]. The usage of natural polymer/tantalum oxide hybrid composites is an important aspect of the green synthesis strategy, which results in finer and more uniform TaC particles than is possible with current commercial production methods.

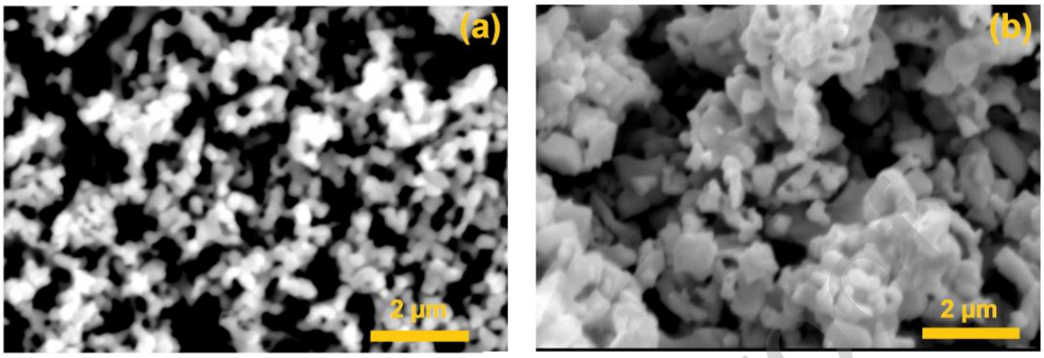

Fig 6. SEM micrographs of (a) as–synthesized and (b) commercial TaC powder.

The X-ray diffraction (XRD) results (Fig. 7 a, b) provide valuable insights into the crystalline phases and lattice parameters of sintered tantalum carbide (TaC) with and without the addition of as-synthesized TaC. In both cases, the XRD patterns exhibited no discernible differences in terms of the phases present, indicating that the addition of as-synthesized TaC did not introduce new phases during the spark plasma sintering (SPS) process. The consistent phase composition reaffirms the purity and stability of the TaC phase in both commercially sintered samples with and without the as-synthesized TaC addition. However, a notable distinction was observed in the lattice parameter measured by the Nelson-Riley function of commercially sintered TaC with the addition of as-synthesized TaC, as depicted in Fig. 7b. The increase in lattice parameter is attributed to the incorporation of carbon (C) from the as-synthesized TaC into the TaC lattice during sintering. This phenomenon is consistent with previous studies that highlight the impact of carbon addition on lattice parameters in carbide materials. The carbon incorporation modifies the crystal structure, leading to an expansion of the lattice parameter. This observation aligns with the expected behavior, where the as-synthesized TaC, with its finer particle size and unique properties, influences the lattice parameters of the commercially sintered TaC matrix. The rise in lattice parameter is indicative of successful incorporation and interaction between the as-synthesized TaC and the commercial TaC matrix, showcasing the potential for tailored material properties through controlled additions [41].

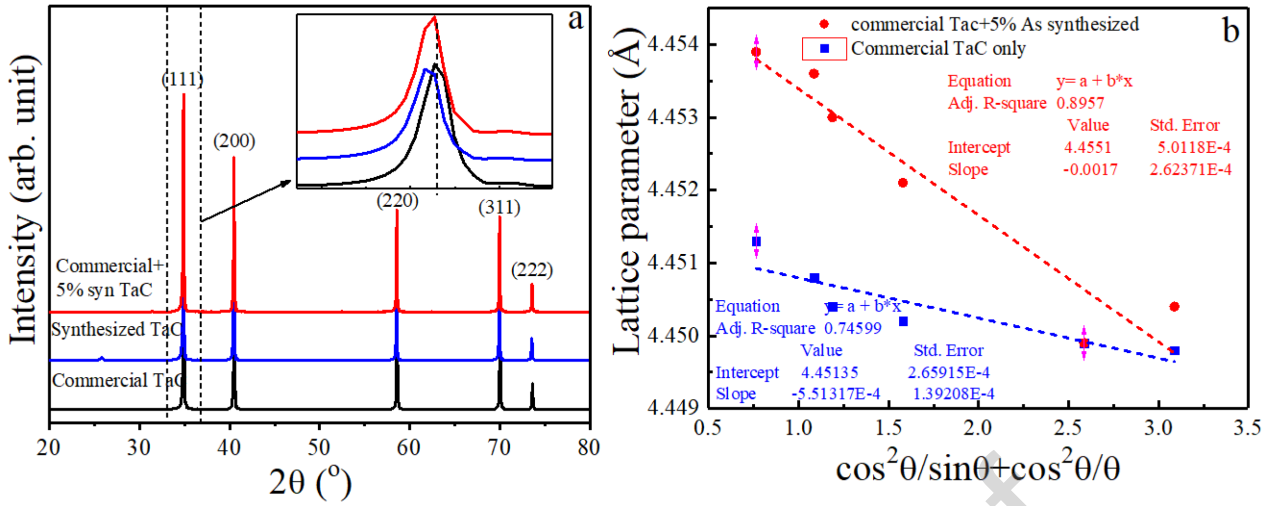

Fig 7.(a) XRD of sintered sample of as-received commercial TaC, as–synthesized TaC and commercial with 5% of as synthesized TaC as an additive, (b) estimation of lattice parameter by Nelson-Riley function for the commercial TaC and with 5% as synthesized TaC as an additive.

At a sintering temperature of 2000 °C, both as-received commercial TaC and commercial TaC with 5% as-synthesized TaC powder additive were subjected to spark plasma sintering (SPS). The SPS profiles, represented as displacement curves versus time (Fig. 1), were analyzed to understand the sintering behavior. Dwelling at the highest temperature for 10 minutes was consistent for both compositions. After cooling from a temperature of 1500 °C, the commercial TaC reached a bulk density of 11.30 g/cm^3, corresponding to only about 78% of the theoretical density. In contrast, the commercial TaC with 5% as-synthesized TaC powder achieved densification starting at 1100 °C, resulting in a density of 14.40 g/cm^3, nearly 98% of the theoretical value. SEM backscattered electron images of the polished surface (Fig. 8a) reveal a microstructure characterized by uniform grains. The surface morphology indicates a degree of densification, but some voids and irregularities are observed, contributing to the lower overall density achieved compared to the theoretical maximum. Fig. 8b illustrates the surface of the sintered samples of commercial TaC with 5% as-synthesized TaC powder additive. The grains appear more uniform and tightly packed, suggesting improved densification compared to the as-received commercial TaC. The enhanced densification is attributed to the additives large surface area of nanometric-sized particles, excellent dispersion, and the presence of free carbon in the as-synthesized powder. The improved sintering density observed in the commercial TaC with 5% as-synthesized TaC powder additive can be justified by several factors. Densification in the presence of as-synthesized TaC powder as an additive initiates at a lower temperature (1100 °C), allowing for an early onset of the sintering process. This contributes to achieving a higher final density compared to the as-received commercial TaC, which starts densification at a higher temperature (1500 °C). The nanometric size of the as-synthesized TaC particles plays a crucial role in enhancing sintering. The large surface area of these particles provides numerous nucleation sites for the sintering process, promoting efficient particle rearrangement and packing. The uniform distribution of nanometric-sized TaC particles in the commercial TaC matrix ensures effective dispersion. This homogeneity contributes to a more uniform microstructure and improved particle packing during the sintering process, ultimately leading to higher density. The presence of free carbon in the as-synthesized TaC powder acts as a sintering aid, facilitating enhanced bonding between particles. The carbon phase assists in reducing voids and promoting a more efficient sintering process, contributing to the higher achieved density. The addition of 5% as-synthesized nanometric-sized TaC to commercial TaC significantly improves sintering density. The early onset of densification, coupled with the nanometric particle size, excellent dispersion, and the presence of free carbon, collectively contribute to the enhanced densification observed in the composite material.

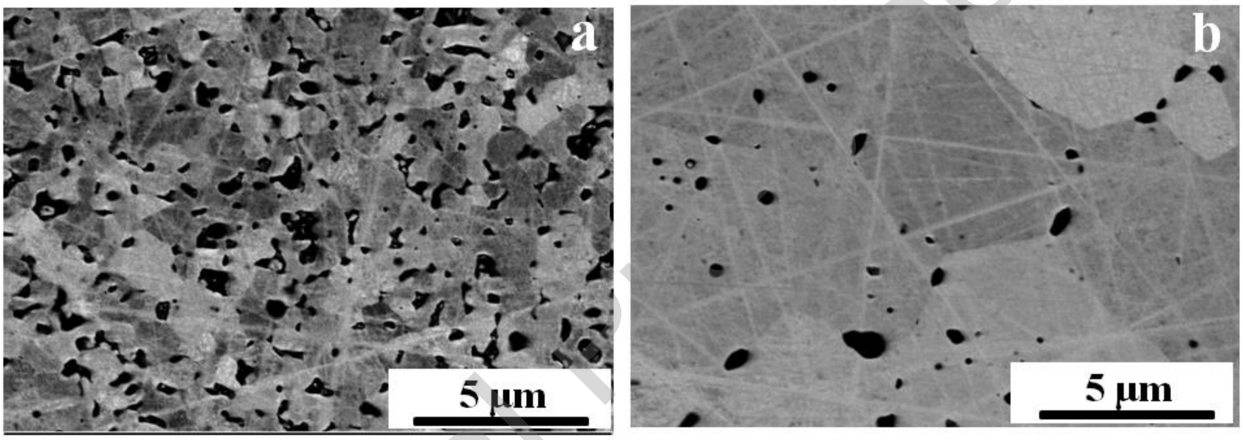

Fig. 8. SEM back scattered electron images of the SPS sintered polished surface of commercial TaC (a) and commercial+5wt% as–synthesized TaC as sintering additive.

One of the primary advantages of utilizing gum karaya in TaC synthesis is its inherent environmental friendliness. As a natural and biodegradable polysaccharide, gum karaya offers a sustainable alternative to synthetic chemicals commonly used in traditional synthesis methods. The utilization of natural precursors like gum karaya reduces the reliance on harsh chemicals and minimizes the generation of hazardous waste and pollutants, thereby contributing to a greener and more sustainable synthesis approach. Furthermore, the synthesis process itself is relatively simple and energy-efficient, operating at moderate temperatures and requiring minimal energy input. This reduces the overall environmental footprint associated with the production of TaC nanoparticles and aligns with the principles of green chemistry.

In addition to its environmental benefits, the incorporation of gum karaya in TaC synthesis leads to enhanced processing and properties of the resulting nanoparticles. The presence of gum karaya as a complexing agent helps to control the size, morphology, and dispersion of TaC nanoparticles, resulting in improved homogeneity and uniformity in the final product. These enhanced properties translate to improved properties of TaC-based materials, making them suitable for a wide range of applications in advanced ceramics, coatings, and nanocomposites.

The green synthesis of nanosized tantalum carbide using gum karaya represents a sustainable and environmentally friendly approach towards producing advanced materials with enhanced properties. By leveraging the unique properties of gum karaya, this method offers a benign and cost-effective alternative to conventional synthesis techniques, while simultaneously improving the processing and properties of TaC nanoparticles. This research contributes to the advancement of green nanotechnology and underscores the potential of natural polymers in facilitating the sustainable synthesis of advanced materials.

Conclusions

In conclusion, this research has effectively showcased the environmentally friendly production of nanoscale tantalum carbide (TaC) by employing carbothermal reduction techniques on hybrid composites of gum karaya and tantalum oxide. The TaC powder that was obtained displayed desirable properties, with an average particle size of 200 nm and a shape that was nearly spherical. One notable characteristic of this synthesis methodology is the commencement of TaC creation at a reduced temperature of 1135 ^{o}C, in contrast to conventional solid-state reduction techniques. Additionally, the investigation examined the pragmatic utilisation of the synthesised TaC through its integration as an addition in commercially available TaC powder. The use of 5% as-synthesized TaC significantly improved the compaction of the commercially available powder, resulting in a noteworthy relative density of 92%. The presented methodology not only demonstrates the inherent capabilities of the synthesised nano powder, but also offers a financially feasible resolution by leveraging its utilisation to enhance the densification of the comparatively costlier commercial alternative. The enhanced densification behaviour seen in the study can be attributed to the nanometric particle size of the synthesised TaC, as well as the presence of a small quantity of free carbon. In general, this study presents a viable and economically efficient approach to producing advanced materials. It highlights the practicality and improved characteristics obtained by employing environmentally friendly methods to synthesise nanosized TaC.

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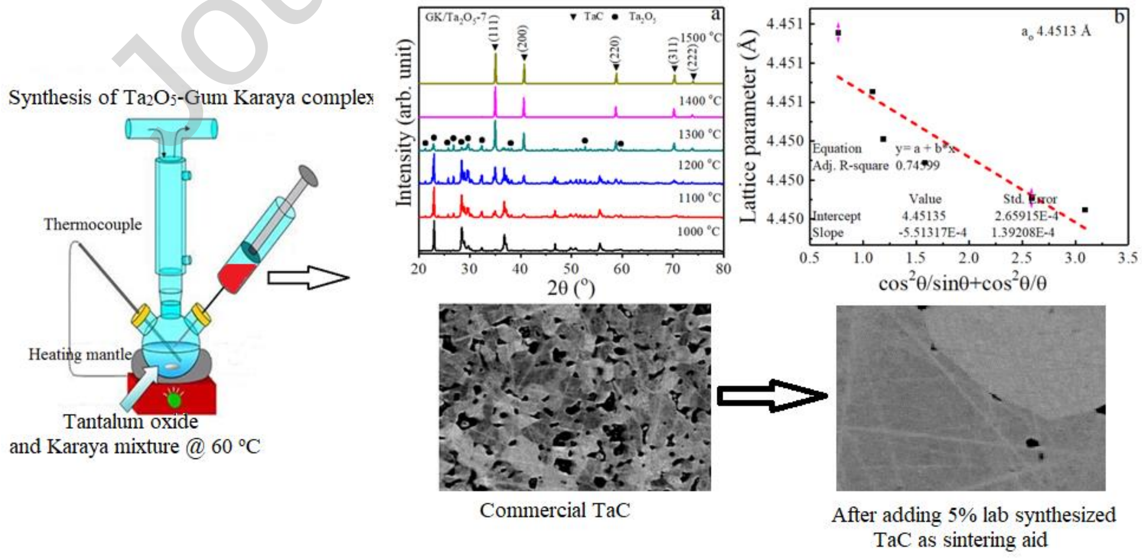
Graphical abstract



Author Statement

We are pleased to submit the revised manuscript titled "Green Synthesis of Nanosized Tantalum Carbide (TaC) via Natural Polymer/Tantalum Oxide Hybrid Composites: A Sustainable Approach towards Enhanced Processing and Properties" for consideration in the Journal of Analytical and Applied Pyrolysis.

In response to the valuable feedback from the reviewers and the editorial team, we have made significant revisions to our manuscript. These revisions primarily focus on enhancing the clarity of the methodology, providing additional experimental details, and addressing the queries raised regarding the characterization techniques employed.

Our study presents a novel and environmentally friendly approach for the synthesis of nanosized tantalum carbide (TaC) utilizing natural polymer/tantalum oxide hybrid composites. We believe that this sustainable synthesis route holds considerable promise for advancing the processing techniques of tantalum-based materials, offering both economic and environmental benefits.

The revised manuscript focuses deeper into the mechanisms underlying the synthesis process, elucidates the role of natural polymers in facilitating the formation of tantalum carbide nanoparticles, and provides a comprehensive analysis of the resulting material properties. Moreover, we have incorporated new explanation and discussions to further support our findings and conclusions.

We are confident that the revised manuscript substantially improves upon the original submission and addresses the concerns raised during the review process. We are grateful for the opportunity to contribute to the Journal of Analytical and Applied Pyrolysis and sincerely hope that our work will be considered for publication.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Utilized green synthesis method involving pyrolysis of natural polymer (Gum karaya)/tantalum oxide hybrid composites for producing nanosized tantalum carbide (TaC), ensuring sustainability and environmental benignity.

- Synthesis methodology initiated TaC formation at a reduced temperature of 1135 °C, contrasting with conventional solid-state reduction techniques, indicating energy efficiency.

- Integration of synthesized TaC as an additive in commercially available powder improved compaction, resulting in a noteworthy relative density showcasing economic feasibility and enhanced densification behavior.

- Overall, the research presents a viable, economically efficient approach to producing advanced materials, emphasizing practicality and improved characteristics achieved through environmentally friendly synthesis methods and materials.