

# NANOMETRIC TANTALUM CARBIDE: PRODUCTION AT LOW TEMPERATURE AND CHARACTERIZATION

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## Abstract

Tantalum carbide (TaC) is an extremely hard material with features such as high hardness, high melting point, high chemical stability, good resistance to chemical and thermal shock and excellent resistance to oxidation and corrosion. Thus, this study aimed to obtain nanostructured TaC from precursor tris (oxalate) hydrate ammonium oxitanalato through gas-solid reaction at low temperature (1000°C) and short reaction time. The materials obtained were characterized by X-ray diffraction (XRD), Rietveld refinement, Scanning Electronic Microscopy (SEM), Infrared Spectroscopy and Thermogravimetric analysis (TG). Through XRD analyses and Rietveld refinement of TaC with  $S = 1.1584$ , the formation of pure tantalum carbide with cubic structure and average crystallite size in the order of 12.5 nanometers was observed.

**Keywords:** Nanostructured tantalum carbide; Oxalic precursors; Gas-solid reaction.

## CARBETO DE TÂNTALO NANOESTRUTURADO: PRODUÇÃO E CARACTERIZAÇÃO À BAIXA TEMPERATURA

## Resumo

O carbeto de Tântalo (TaC) é um material extremamente duro, apresentando elevada dureza, elevado ponto de fusão, elevada estabilidade química, boa resistência ao ataque químico e choque térmico e excelente resistência à oxidação e corrosão. Desta forma, este trabalho teve como objetivo a obtenção de TaC nanoestruturado a partir do precursor tris(oxalato)oxitanalato de amônio hidratado, através de reação gás-sólido a baixa temperatura (1000°C) e curto tempo de reação. Os materiais obtidos foram caracterizados através de difração de Raios-X (DRX), Refinamento Rietveld, Microscopia Eletrônica de Varredura (MEV), Espectroscopia de Infravermelho (espectroscopia IV), Termogravimétrica (TG). Através das análises de DRX e do refinamento Rietveld para o TaC com  $S = 1,1584$  observou-se a formação do carbeto de tântalo puro com estrutura cúbica e tamanho médio de cristaltos na ordem de 12,5 nanômetros.

**Palavras-chave:** Carbeto tântalo nanoestruturado; Precursores oxálicos; Reação gás-sólido.

## 1 INTRODUCTION

There has been a significant growth of studies on the production and characterization of ultrafine and nanostructured materials, which has attracted fundamental and technological research in recent years due to the possibility of improvement of various properties of nanostructured materials compared to materials obtained by conventional methods. These new methods have also been applied in the synthesis of refractory metals carbide, which have been developed to produce carbides with suitable properties for using in high-quality cemented carbides production and more selective catalysts.

Carbides are binary carbon compounds classified according to the available type of chemical bonding in their formation that can be ionic, covalent or metallic. These carbides have great technological importance, such as high melting point, good wear resistance and extreme hardness. Due to these factors, they have great applicability as special matrixes in the aerospace, military, metallurgy and chemical industries, and in the development of cemented carbides, which are composed of high-hardness carbides and a binding metal as binder [1].

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Tantalum carbide (TaC) is an extremely hard material; It often adds to the WC/Co composite to enhance the physical properties of the sintered structure; acts as a grain growth inhibitor, preventing the formation of large grains and produces with material excellent hardness; It is used a coat for steel molds in molding by injection of aluminum alloys; in the production of cutting tools with high mechanical strength and hardness; and is used as drills for cutting tools. It is a metallic brown-gray powder highly resistant to corrosion. Tantalum carbide has CFC crystalline structure, high hardness, comparable to that of NbC and VC, and high melting point (about 3880°C). It can be produced by heating a mixture of Ta and C (reaction dependent on solid state diffusion) or by heating a mixture of C and Ta<sub>2</sub>O<sub>5</sub> (reduction of solid waste reagents followed by carburizing). The latter method is more common.

This study aimed to synthesize precursor tris (oxalate) hydrate ammonium oxitantalato and tantalum carbide by gas-solid reaction in a tubular furnace at low temperature and short reaction time and characterize them through X-ray diffraction (XRD), Rietveld refinement, Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TG) and Infrared Absorption Spectroscopy (IR).

## 2 MATERIALS AND METHODS

Based on methodology of Medeiros [2] precursor tris (oxalate) hydrate ammonium oxitantalato was produced by using 4 g of tantalum oxide and 40 g of potassium bisulfate weighed on an analytical scale and mixed with Ta<sub>2</sub>O<sub>5</sub> and KHSO<sub>4</sub> at ratio of 1:10 by using mortar and pestle. Subsequently, merger was performed in platinum crucible resistant to high temperatures by using a Bunsen burner. After the completion of the merger, a homogeneous, purple liquid was obtained. The liquid was transferred to a porcelain container to be cooled and crystallized. The solidified material was triturated by using mortar and pestle to obtain a homogenous powder of small grain size.

Then, about 80 mL of concentrated and hot sulfuric acid were added. Approximately 325 mL of ammonium hydroxide were added by using a burette until pH reached value between 8 and 9. Subsequently, washing was performed

with 1% acetic acid solution and then complexation was done at 65°C with a solution of oxalic acid and ammonium oxalate with a ratio of 1: 3 between tantalum and oxalate ions, and after complexation, the resulting solution was kept for 24 hours. The solution water was evaporated at 80°C, giving origin to the precursor, a crystalline solid that was triturated by using mortar and pestle to obtain a homogenous powder of small grain size and dried in greenhouse for 24 hours.

Tantalum carbide was produced at low temperature (1000°C) from precursor tris (oxalate) hydrate ammonium oxitantalato macerated in a mortar. Hydrogen (H<sub>2</sub>) and methane (CH<sub>4</sub>) were used as reducing gases and carbon source, respectively. The reactions between precursor and mixture of methane and hydrogen were performed in a resistive furnace, consisting of alumina fixed bed reactor. To accommodate the precursor sample in the fixed bed reactor, a little alumina boat was used and all assays used a mass of 2 grams, which was introduced into the alumina tube and placed at the central part of the furnace. After closing the tube, it was rinsed with argon for several minutes to remove all oxygen. Then, the flow of reactant gases (methane and hydrogen) was adjusted and the gas mixture was circulated through the reactor.

Decomposition-reduction-carburization reactions were conducted at 1000°C and isotherm time of 120 minutes. Flow rates of 1 L/h of methane and 19 L/h of hydrogen, related to 5% and 95% of the gas flow mixture respectively [2] were used. At the end of the decomposition-reduction-carburization reaction, the flow of reactant gases was changed to an argon flow (10 L/h) and this flow was maintained until room temperature was achieved, when the samples were taken.

Based on studies of carburization reduction of the niobium precursor and thermoanalytical studies performed by Medeiros [2], it is possible to propose steps carburizing decomposition-reduction reactions involved in the synthesis of TaC, as described in the following equations in the Figure 1.

In equation 2 of the Figure 1, the formed oxide (Ta<sub>2</sub>O<sub>5</sub>) is reduced by hydrogen in TaO<sub>2</sub> then carburated by methane producing tantalum carbide (TaC). In the synthesis of TaC, methane acts as a reducing reacting with TaO<sub>2</sub> forming CO and simultaneously reacting with the tantalum producing TaC.

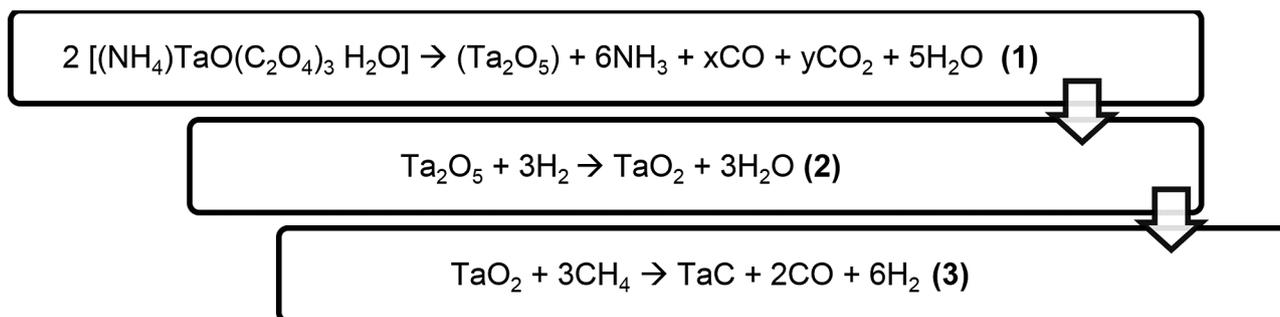


Figure 1. Flowchart of reactions involved in the synthesis of TaC.

### 3 RESULTS AND DISCUSSION

#### 3.1 Characterization of the Oxalic Tantalum Precursor

Oxalic tantalum precursor was characterized by thermogravimetric analysis (TG), infrared absorption spectroscopy (IR) and scanning electron microscopy (SEM).

##### 3.1.1 Infrared absorption spectroscopy of the precursor

Figure 2 shows the absorption spectrum in the infrared region of oxalic Ta precursor. The spectrum shows broad absorption band of intermediate intensity in the region from  $3400\text{ cm}^{-1}$  to  $2950\text{ cm}^{-1}$  at about  $3150\text{ cm}^{-1}$ , which may be attributed to the stretching mode  $\nu$  (OH) of hydration water [3]. The band presented in the region from  $1800\text{ cm}^{-1}$  to  $1550\text{ cm}^{-1}$  at approximately  $1790\text{ cm}^{-1}$  refers to oxalate groups coordinated to tantalum. The symmetric and asymmetric stretching modes observed at  $1790\text{--}2925\text{ cm}^{-1}$  correspond to vibrational modes of the oxalate group. In the regions of  $1360\text{ cm}^{-1}$  and  $1235\text{ cm}^{-1}$ , bands refer to ionic groups C-O and C=O, a fact that accentuates the coordinating of oxalate groups to tantalum. Two intense bands at  $690$  and  $890\text{ cm}^{-1}$  were also observed in the spectra and can be assigned to coordination between metal ions, in this case Ta, with oxalate ion sites (Ta-O and Ta = O) [4]. However, infrared spectroscopy revealed vibration bands of O-H, C=O, C-O, O-C = O, and Ta-O groups.

##### 3.1.2 (TG/DTG) Analyses of the precursor

Through the TG / DTG results shown in Figure 3 and Table I for precursor tris(oxalate) hydrate ammonium oxitantalato, it could be observed that weight loss occurred in three main steps. The first weight loss occurs in the range from  $25^\circ\text{C}$  to  $110^\circ\text{C}$ , which corresponds to the dehydration process (2.065% by mass is equivalent to 0.1097 mg). From  $110^\circ\text{C}$  to  $800^\circ\text{C}$ , two major losses equivalent to 61.39 wt%, corresponding to 3.26 mg of weight occurred. The second weight loss occurring between  $110^\circ\text{C}$  and  $400^\circ\text{C}$  corresponds to decomposition of oxalate with release of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{NH}_3$ . The third weight loss event occurs in the range from  $650^\circ\text{C}$  to  $800^\circ\text{C}$  with small weight loss of 1.7% corresponding to 0.09 mg, which can be attributed to the evolution of  $\text{CO}_2$  and crystallization of the decomposed material; however, this evolution is not the result of decomposition of the tantalum complex,

according to Marta et al. [5]. Thus, this event can be assigned to desorption of the gas produced at low temperature and adsorbed on the material surface. From  $800^\circ\text{C}$ , no significant weight loss was observed. Therefore, the study on thermal decomposition by TG/DTG shows total weight loss of 65.66% with total loss of 3.488 mg.

##### 3.1.3 Scanning Electronic Microscopy (Sem) analysis of the precursor

The physical aspects of tantalum precursor were observed by scanning electron microscopy (SEM), with magnification of 1500x, 5000x and 15000x, shown in Figure 4a-d. Through SEM images shown in Figure 4a, b,

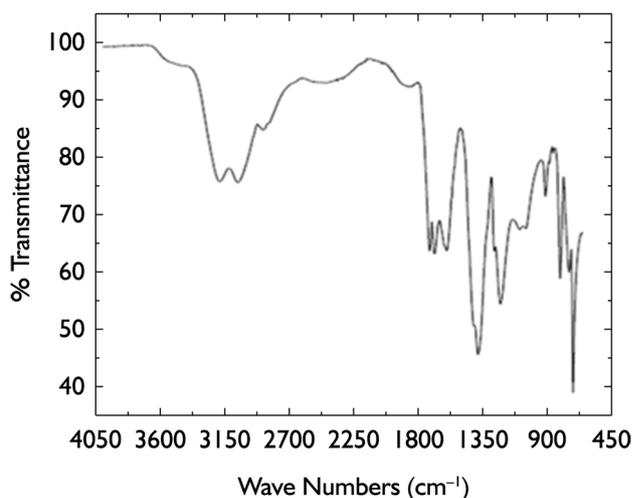


Figure 2. Infrared spectrum of precursor tris(oxalate) hydrate ammonium oxitantalato.

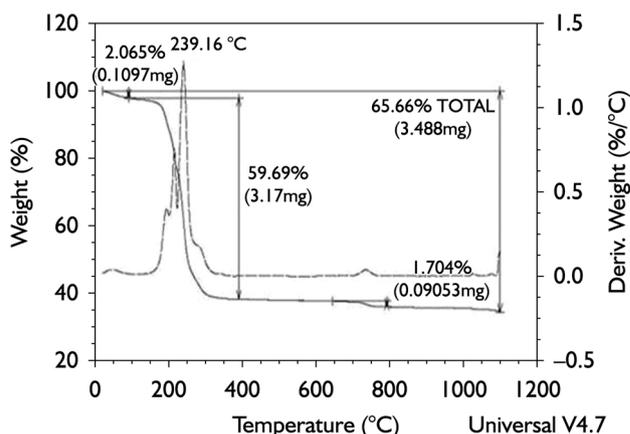
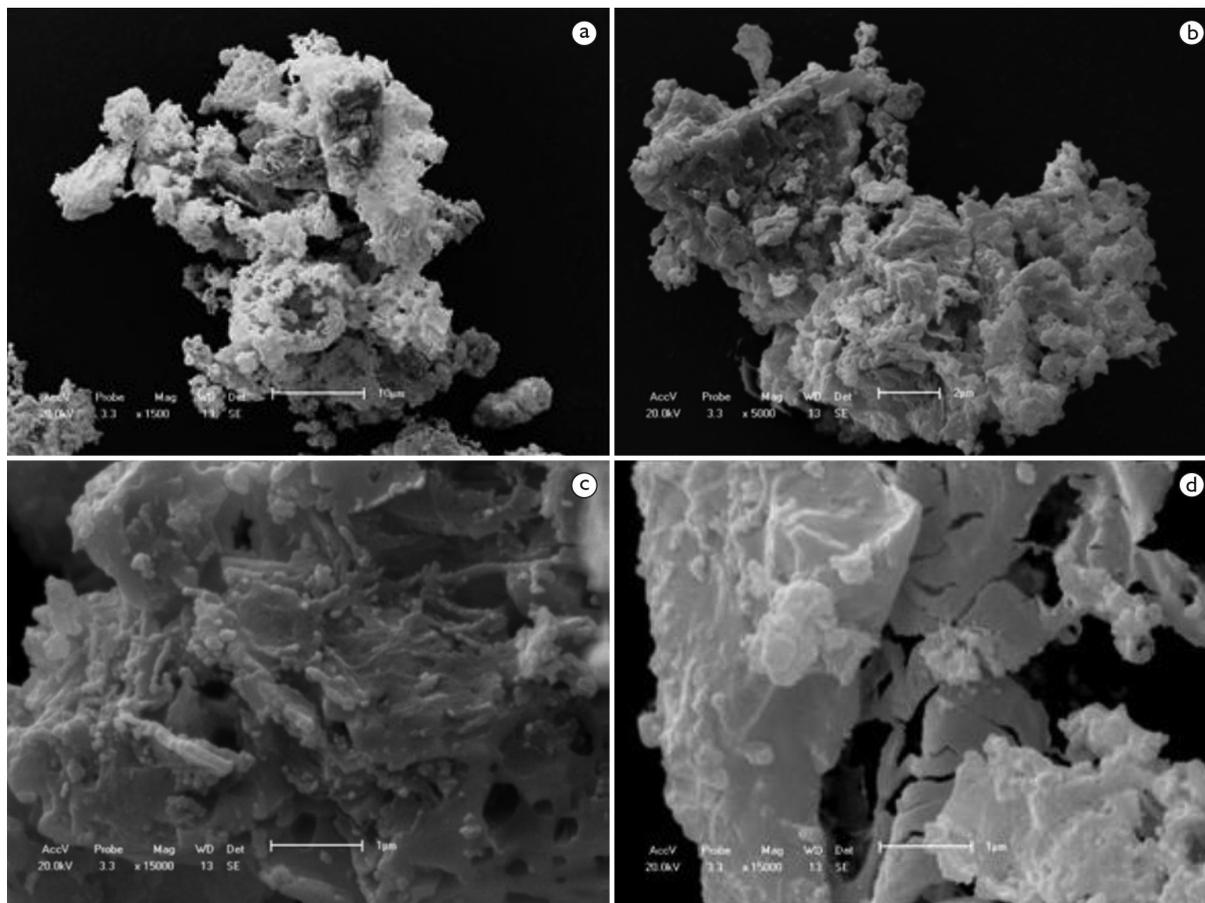


Figure 3. TG / DTG of precursor tris(oxalato) hydrate ammonium oxitantalato.

Table I. TG results of  $(\text{NH}_4)_3[\text{TaO}(\text{C}_2\text{O}_4)_3]\cdot\text{H}_2\text{O}$

Material	Steps	$T_i$ ( $^\circ\text{C}$ )	$T_f$ ( $^\circ\text{C}$ )	$\Delta$ Weight (%)
$(\text{NH}_4)_3[\text{TaO}(\text{C}_2\text{O}_4)_3]\cdot\text{H}_2\text{O}$	1	25	110	2.065
	2	110	400	59.69
	3	625	800	1.704



**Figure 4.** Scanning Electron Microscopy (SEM) of precursor oxalic tantalum (1500x (a), 5000x (b) and 15000x (c and d)).

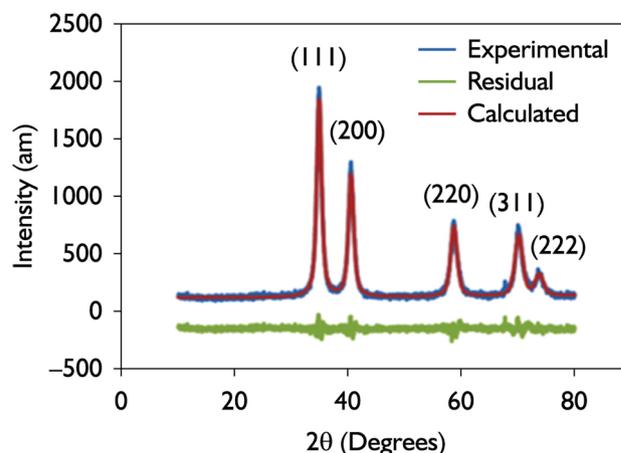
it could be observed that the precursor powder obtained in this work has large particles composed of agglomerates consisting of small crystallites.

Figure 4c, d show that some agglomerated particles have various shapes, some of spherical shape and others in the form of thin plates with few cracks, to Figure 4d, also shows the presence of well-defined pores in Figure 4c. This porosity is responsible for increasing the contact area between solid and gas, promoting the carburization reaction faster and at temperature well below those used in traditional methods, when it is used with the precursor for the production of carbide.

### 3.2 Characterization of Nanometric Tantalum Carbide

#### 3.2.1 XRD and rietveld method

The results obtained by XRD after the carburization process indicated the formation of tantalum carbide, with intensities in the diffraction angles, showing that experimentally produced TaC are pure. Rietveld refinement indicated the presence of tantalum carbide of face-centered cubic structure (CFC), and allowed determining the crystallographic parameters of samples and the deviation from literature data and the average particle size.



**Figure 5.** Diffraction Spectrum of X-rays refined by the Rietveld method.

Figure 5 shows the experimental pattern of X-ray diffraction of carbides, identifying the characteristic TaC peaks. This shows that the process of gas- solid synthesis adopted in this study was effective. As can be seen, the synthesis of TaC presents characteristic peaks and CFC structure. Moreover, broad peaks are observed, which features the formation of nanostructured tantalum carbide. Table 2 shows the refinement data for revealing the formation of the TaC

crystal in the cubic shape and the following crystallographic parameters:  $A$  ( $a$ ) = 4.4495564  $\text{\AA}$   $b$  ( $\text{\AA}$ )  $c$  = 4.4495564 ( $a$ ) = 4.4495564.  $\text{Alpha}$  ( $^\circ$ ) = 90.0000,  $\text{Beta}$  ( $^\circ$ ) = 90.0000,  $\text{Gamma}$  ( $^\circ$ ) = 90.0000, face-centered cubic crystal structure, the cell parameters ( $a$ ,  $b$ ,  $c$ ) are equal. Thus, the TaC FCC presents its cell parameters equal ( $a = b = c$ ). It was also obtained a deviation of  $S = 1.1584$  and average crystallite size equal to 12.9 nm. Table 3 presents some of the main data related to refinements performed for tantalum carbide.

Measurements of the crystallite size and microstrain of TaC powder were performed. The results of these

measurements are shown in Tables 3 and 4. As can be seen, synthesized TaC has crystallite size in the order of nanometers. Furthermore, microstrain values are negligible.

### 3.2.2 SEM of tantalum carbide

Through experimental tantalum carbide micrographs obtained by SEM, Figure 6a, b, it was observed that the product resulting from precursor carburization with gas-solid reaction has mostly uniform morphology, with large particles formed of small and fine particles, some connected and some not.

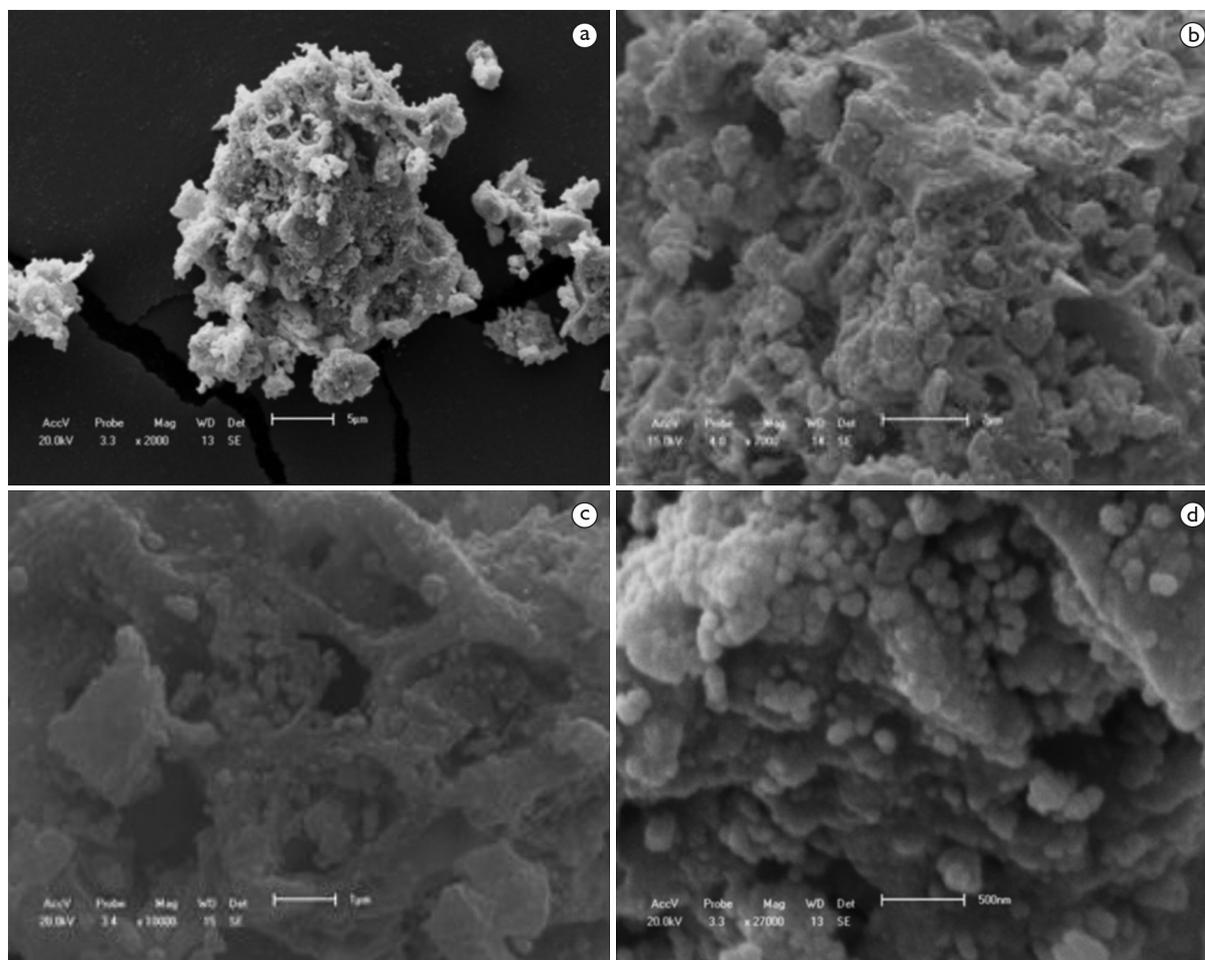
**Table 2.** Refinement data of tantalum carbide by Maud Software

Density	Cell parameters	Crystallite size	Structure	Phase
14.5 $\text{g/cm}^3$	4.4495564 $\text{\AA}$	12.9 nm	CFC	44497-ICSD

**Table 3.** Results of the average crystallite size obtained by the Scherrer method

Material	TaC					
Position ( $2\theta$ )	34.856	40.478	58.617	70.078	73.697	Tm(medium) (nm)
Tm (nm)	9.1929	8.8137	7.9115	7.5362	7.4402	8.179

Tm = Average crystallite size.



**Figure 6.** Scanning electron microscopy (SEM) of tantalum carbide (2000x (a), 7000x (b), 10000x (c) and 27000x (d)).

**Table 4.** Results of the average crystallite size and microstrain obtained by the Williamson-Hall method

Material	Tm (nm)	Md (%)
TaC	12.05	0.003250

Tm = Average crystallite size; Md = microstrain.

Fine particles, usually at the nanoscale, have large surface areas and often, in an attempt to minimize the total surface area or the system interface energy, agglomerate, forming secondary particles [6]. Figure 6, b show that particles are large and porous and are formed of agglomerates of small particles. This analysis is in agreement with the result obtained by the refinement of structure containing TaC with average crystallite size of 12.9 nm, as results shown in Table 2. Figure 6c, d show that the morphology of particles present disordered grains, which is characteristic of nanoscale materials. Morphology with aspect of small aggregated and dispersed plates is also observed.

#### 4 CONCLUSION

The use of oxalic precursor developed in this work has higher reactivity compared with commercial tantalum oxide for the synthesis of TaC. Thus, this precursor can be used in TaC synthesis at much lower temperatures and reaction times compared to those used in conventional

synthesis. For the conventional method, the tantalum carbide is obtained at temperatures ranging from 1300°C to 1500°C, however, in order to have a good homogeneity of the final product, high temperatures around 2000°C throughout the reaction is necessary. However the method used in this work allowed to produce tantalum carbide at 1000°C and an isotherm of two hours. Thus the method of synthesis of oxalic tantalum precursor is seemed to be appropriate, increasing the reactivity during the carburizing reaction to produce TaC.

The results presented for TaC revealed the formation of pure phase with characteristics different from those conventionally obtained such as particle size and average crystallite size in the nanometer order, reaching 12.05 nm. These features allow the use of carbide not only as reinforcement in hard metal and manufacturing of alloys, but also as a catalyst. However, future studies should be carried out to confirm its possible application as catalysis.

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