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Elaboration of mixed tantalum and niobium carbides from tantalite mineral $(Fe,Mn)(Ta_{1-x}Nb_x)_2O_6$

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This paper presents an original method of synthesis of mixed tantalum and niobium carbides from an oxalic precursor elaborated from the tantalite mineral $(Fe,Mn)(Ta_{1-x}Nb_x)_2O_6$. The process of elaboration consists initially in melting the ore with potassium pyrosulphate, then performing a lixiviation with a concentrated hydrochloric acid solution. During the latter reaction, iron and manganese oxides are converted into water-soluble chlorides while the fused mass containing potassium, niobium and tantalum is not dissolved. Traces of chlorides are eliminated by filtration with boiling aqueous solution. Then, the solid is dissolved slowly in hot concentrated sulphuric acid solution. Adding ammonium hydroxide up to a pH of 8 completes the precipitation of niobium and tantalum hydroxides. The precipitate $(Ta_{1-x}Nb_x)(OH)_5$ is washed and submitted to a reaction of complexation with oxalate ions in an aqueous environment. This reaction involves the formation of a water-soluble oxalic complex containing tantalum and niobium. The excess of water is eliminated by evaporation at 333 K. The tantalum and niobium carbides are obtained by submitting the oxalic complex of chemical formula $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$ to a gas-solid reaction in a methane-hydrogen atmosphere at 1273 K. The oxalic precursor and their resultant mixed carbides are characterized by atomic absorption and Infra-Red spectroscopies, thermogravimetric-differential thermal analysis coupled, laser granulometry, X-ray diffraction and transmission electronic microscopy. © *2002 Kluwer Academic Publishers*

1. Introduction

Due to their physicochemical properties, interests in the manufacturing of the niobium and tantalum carbides are growing up for industrial applications.

The classical manufacturing route for the synthesis of those carbides is based on the solid-state diffusion of the carbon in the transition metal. The process is activated by high temperature treatment up to 1473 K for long periods of time [1, 2]. Among all the minerals in which tantalum and niobium are found, the main source is the tantalo-columbite mineral $(Fe,Mn)(Ta_{1-x}Nb_x)_2O_6$ where they occur in combination with iron and manganese.

Previous works focused on the direct carburization of tantalo-columbite concentrate $(Fe,Mn)(Ta_{1-x}Nb_x)_2O_6$ [3, 4], however the temperature reached 1673 K for few hours.

An alternative route to decrease the temperature and the time of synthesis of tantalum and niobium carbides consists of the carburization of an oxalic precursor. This method has been applied successfully in the preparation of TaC [5] and NbC [6] from tantalum and niobium pentoxides as raw materials.

This study extends the process to the elaboration of a mixed tantalum-niobium carbide: the oxalic precursor is elaborated from tantalite mineral and then submitted to the carburant atmosphere.

The first part of the present contribution reports the different steps of the synthesis of the precursor: the melting of the mineral with potassium hydrogen sulphate ($KHSO_4$), the elimination of iron and manganese by hydrochloric acid dissolution, the precipitation of niobium and tantalum hydroxides by ammonia addition, the complexation of hydroxides by an equimolar mixture of oxalic acid and ammonium oxalate and the characterization of the precursor.

The second part of the study carries on the conditions of carburisation of the precursor under a flowing atmosphere of methane and hydrogen.

2. Experimental procedure

2.1. Materials

Potassium hydrogen sulphate ($KHSO_4$), oxalic acid dihydrated ($H_2C_2O_4 \cdot 2H_2O$), ammonium oxalate monohydrated ($(NH_4)_2C_2O_4 \cdot H_2O$) were obtained from Aldrich. Gases employed are methane (purity: 99%) and hydrogen (high purity grade). Tantalite mineral is not a commercial product.

2.2. Elaboration of the ammonium oxalato tantalo-niobate

2.2.1. Characterization of the tantalite mineral

The starting material is an ore extracted in the region of Rio Grande do Norte in the North-East of Brazil. All organic substances and slurries have been eliminated from the ore by flotation and gravitation, before being used in the experiment [7].

The X-ray diffraction pattern of the mineral in Fig. 1 determines the classical tantalite mineral identified by the J.C.P.D.S file number 33-0659 [8].

Its chemical composition gives a content of niobium lower than 2% in mass and resumed in Table I.

TABLE I Chemical composition of tantalite mineral

Elements	%
Ta	73
Nb	∠2
Fe	16
Mn	9

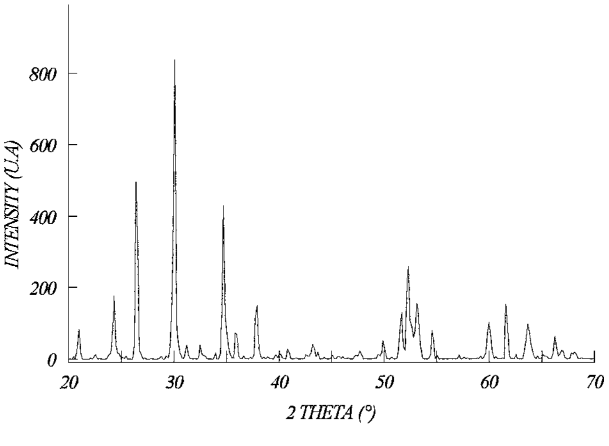


Figure 1 X-Ray diffraction pattern of the tantalite mineral.

2.2.2. Elaboration of the oxalic precursor $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$

The guiding idea is to operate the decomposition of the mineral with potassium hydrogen sulphate ($KHSO_4$) leading to a reactive solid compound in which potassium, niobium, iron and manganese are intimately mixed, and after, eliminate the minor constituents in soluble water chlorides by dissolution in hydrochloric acid.

The melting of the mineral was made with potassium hydrogenosulphate according to the method developed in precedent works [9–13].

So, the mineral was ground with the potassium hydrogenosulphate in proportion 1 : 7 in mass and heated in a platinum crucible with help of a Bunsen burner. During the melting, potassium hydrogen sulphate ($KHSO_4$) decomposes in potassium pyrosulphate as intermediate, and sulphur trioxides [14, 15] as shows the following equations:

$$2KHSO_4 \Rightarrow 2K^+ + 2HSO_4^- \Rightarrow 2K^+ + H_2O + S_2O_7^{2-} \Rightarrow H_2O \uparrow + K_2S_2O_7 \quad (1)$$

$$K_2S_2O_7 \Rightarrow K_2O + 2SO_3 \uparrow \quad (2)$$

The heating is pursued until no releasing of gases is detected and all the material becomes a clear reddish homogeneous liquid.

After cooling down to room temperature, the mass is ground and added to a boiling concentrated hydrochloric acid solution. This operation converts iron and manganese into soluble chlorides, which can be eliminated from the material by filtration.

The entire elimination of iron and manganese is verified by testing the presence of iron and manganese ions in the filtrate with colorimetric tests using ammonium thiocyanate for ferrous ions, orthophenantroline for ferric ions and sodium bismuthate for manganese ions [16]. A washing let to avoid all contamination of the product by chlorides. The resultant insoluble compound of tantalum, niobium and potassium of uncertain composition is slowly dissolved in a hot concentrated sulfuric acid solution.

Bringing the pH of the solution to 8 with ammonia addition performs the precipitation of the tantalum and niobium hydroxides. The precipitate is washed until no trace of potassium ions is detected in the filtrate. The latter step of the process is the complexation of the tantalum and niobium hydroxides by a mixture of oxalic acid and ammonium oxalate. As the higher tantalum quantity is, the slower is the kinetic of the reaction and according to the composition of this tantalite; the reaction of complexation is made under stirring during 12 hours. This reaction involves the formation of a soluble oxalic complex in which tantalum and niobium are intimately mixed at molecular level. The solution is then evaporated at 333 K in a drying oven to give a precursor in powder form.

This one was characterized by atomic absorption and I. R. T. F spectroscopies, X-Ray diffraction and thermal thermogravimetric-differential analysis.

2.2.3. Characterization of the oxalato tantalo-niobate d'ammonium

2.2.3.1. Chemical analysis. In addition to the analytical tests on the filtrate, qualitative analysis is made on the complex. At first, the preliminary analysis consists in the qualitative determination of iron by atomic absorption spectroscopy.

Indeed, precedent trials point out the difficulty to remove iron from the mineral [17], while manganese is readily eliminated. So, in order to prove the purification of the precursor, the chemical analysis focuses only on the iron content in the complex. It was carried out with a Spectra AA—10 Plus VARIAN atomic absorption spectrometer. The results, resumed in the Table II, show traces of iron in the oxalic precursor.

2.2.3.2. Infra-red spectroscopy. The sample was prepared using potassium bromide (KBr) pellet compacted at 10 t/cm^2 with 1% in mass of $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$. The measurement was made with a Matson Unicam spectrometer and the I.R.T.F spectrum is given in Fig. 2.

The indexations of the different bands of vibration are resumed in the Table III.

The assignments of the characteristic vibrations of the oxalic complex are determined according to [18, 19].

The bands due to the oxalato groups coordinated to the tantalum atom occur at wave numbers close to 490 cm^{-1} and 600 cm^{-1}.

The shift of the C=O and the C–O band of the oxalato group are observed in the infrared spectrum.

The crystallisation water molecules produce bands at 3400–3500 cm^{-1}.

TABLE II Quantitative determination of iron by atomic absorption spectroscopy

Sample	Conc. (ppm)
1	0.54
2	0.55
3	0.56

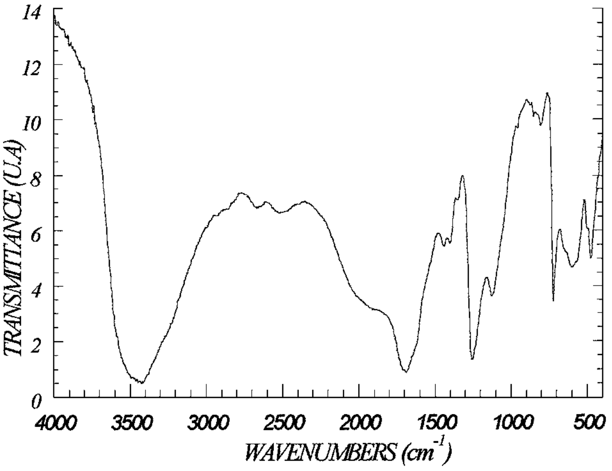


Figure 2 I.R.T.F spectrum of $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$ complex.

TABLE III Characteristics of vibrations in the complex

ν (cm^{-1})	Identification
3400–3500	ν (O—H)
1700–1720	ν (C=O)
1660	ν (C=O)
1250	ν (C—O) et δ (O—C=O)
720	ν (C—C)
600	ν(Nb—O) et ν (Ta—O)
490	δ (O—C=O) et ν(Nb—O)

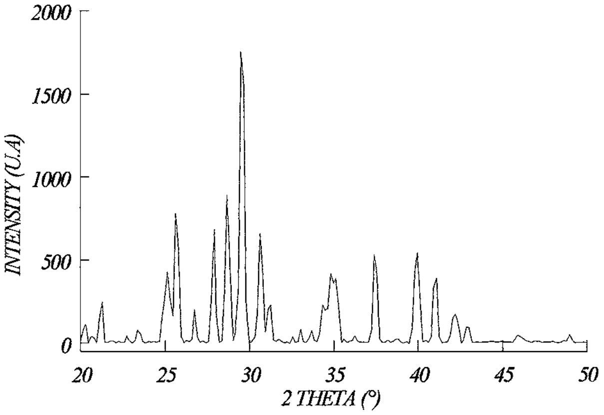


Figure 3 X-Ray diffraction pattern of $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$ complex.

2.2.3.3. X-Ray diffraction characterization of the oxalic complex. The X-ray diffraction pattern shown in Fig. 3 was made with a SIEMENS D 5000 diffractometer on the precursor in powder form.

The X-Ray diffraction pattern of the precursor shows a good crystallinity at room temperature. It was examined with accuracy by the study of the evolution of the X-ray diffraction patterns with temperature.

It was increased by 50 K from room temperature to 1173 K and all the patterns were registered after 40 minutes of stabilisation. The angles of Bragg are given in theta degree. The profile is given in Fig. 4.

It shows that the complex becomes amorphous up to 373 K. The diffraction layers of the pentoxides of niobium and tantalum appear at temperature up to 873 K.

2.2.3.4. Characterization by differential thermal-thermogravimetric analysis (D.T.A-D.T.G). The decomposition of the oxalic complex has been studied by D.T.A-D.T.G with a heating rate of 5 K/min from room temperature to 973 K in a flowing air atmosphere. The curves are given in Fig. 5.

The thermal analysis shows that the decomposition proceeds at various stages associated with endothermic phenomena. Those endothermic peaks are assigned to the dehydratation of the complex and consequently the decomposition of the oxalic complex by releasing of water, ammonia, carbon monoxide and carbon dioxide leading to tantalum and niobium oxide. This is confirmed by no mass loss on the thermo gravimetric analysis up to 620 K.

As no phenomena is detected on the D.T.A and D.T.G signals up to 620 K, we can suppose that the decomposition is achieved at this temperature.

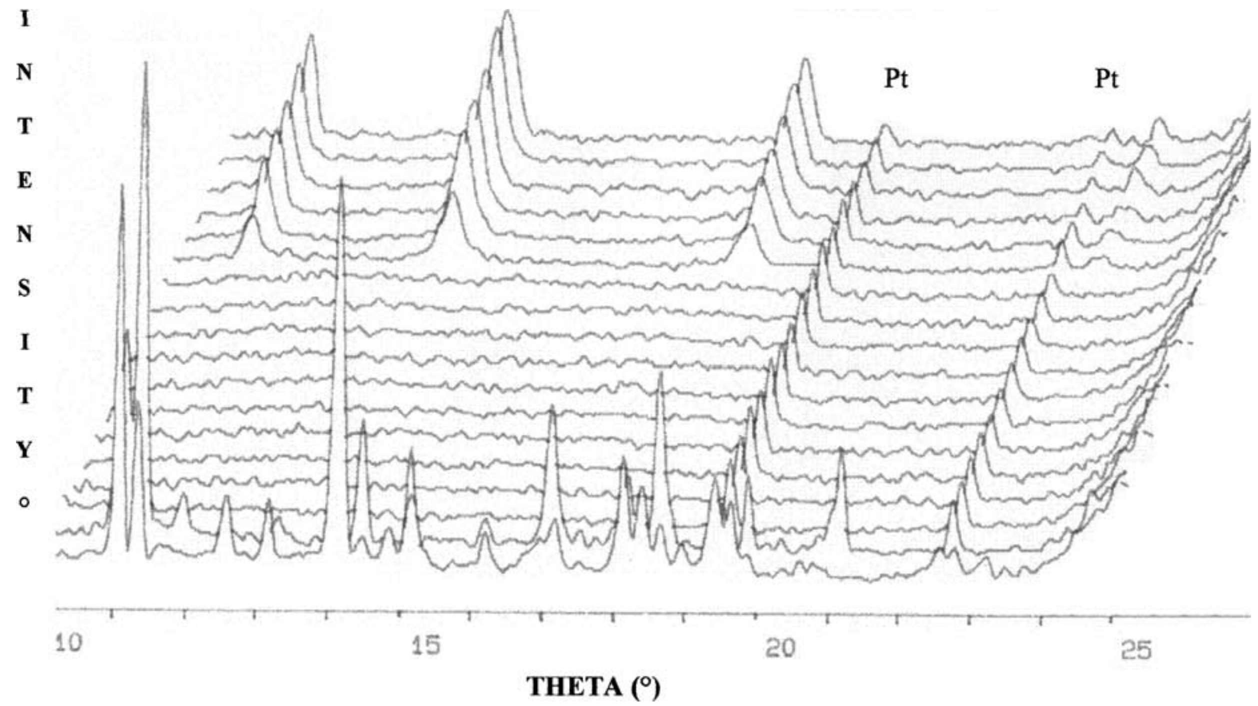


Figure 4 Evolution of the X-Ray diffraction patterns with temperature.

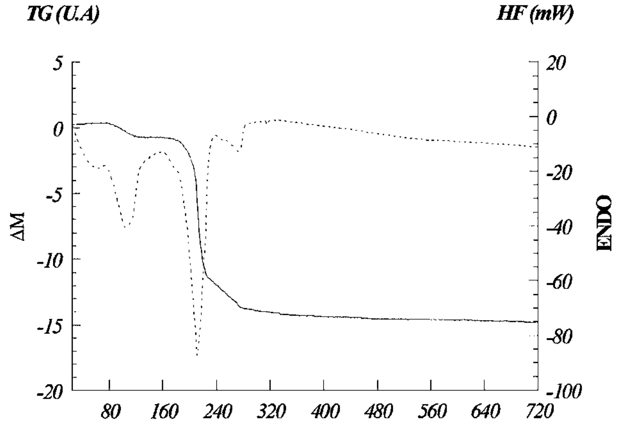


Figure 5 TG-DTA thermograms of $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$ complex.

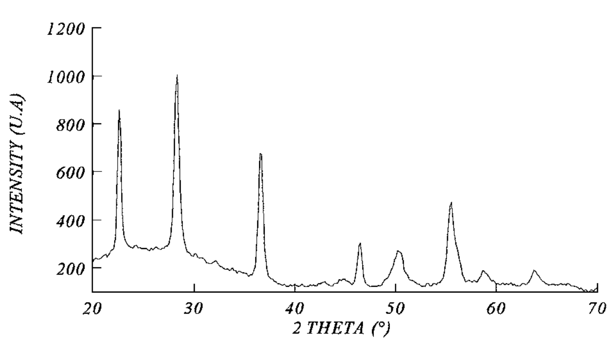


Figure 6 X-Ray diffraction pattern of the phase obtained at 620 K.

The identification of the X-Ray diffraction pattern of the phases obtained after the pyrolysis of the complex at 620 K at a heating rate of 5 K/min is shown on Fig. 6.

The phases obtained, identified by the J.C.P.D.S files number 79-1375 reveal the presence of tantalum pentoxide (Ta_2O_5) [20].

From the complexity of the decomposition of the ammonium oxalato tantalo-niobate, complementary analysis focused on the gases evolved during the pyrolysis of the precursor by I.R.T.F technic was employed.

2.2.3.5. Analysis of the reaction of decomposition by infrared spectroscopy of gases. The I.R.T.F analysis of the gases evolved during the thermolysis let to differentiate the stages of the decomposition. The manipulation is effected in dynamic argon atmosphere to carry on the gases toward the cell of the spectrometer. The heating rate used in this experiment is 5 K/min. The evolution of the gases detected is shown in Fig. 7a–c.

The characterization shows that the gases issued from the thermal decomposition of the complex are water, ammonia, carbon monoxide and carbon dioxide [21–25].

Indeed, the Fig. 7a shows the releasing of ammonia identified by the presence of a singlet at ν $NH_3 = 1623$ cm^{-1} and a doublet of major absorbance at ν $NH_3 = 970$–980 cm^{-1} in the temperature range of 403 K–673 K.

Simultaneously, from 403 K to 673 K, the absorbance peaks at $\nu = 2320\,cm^{-1}$ and $\nu = 2120$–$2180\,cm^{-1}$ show respectively the releasing of carbon dioxide, correlated by the doublet at $\nu = 2120$–2180 cm^{-1} of lower absorbance, significant of the presence of trace of carbon monoxide issued from the decomposition of oxalate species in Fig. 7b.

The dehydratation of the oxalic complex occurs in the temperature range of 403 K–703 K as it showed by the broad absorbance peak between 3000–3700 cm^{-1} in Fig. 7c.

From those data, we can propose a mechanism for the decomposition of the oxalic complex

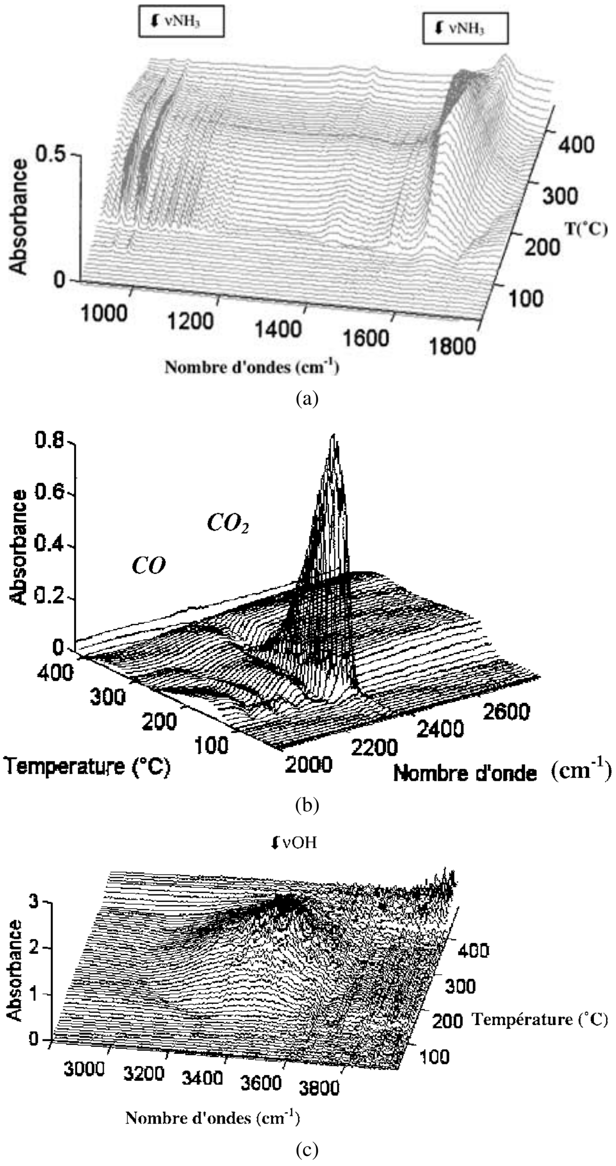


Figure 7 (a) I.R.T.F spectrum of the gases evolved during the thermolysis of the $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$ complex. (b) I.R.T.F spectrum of the gases evolved during the thermolysis of the $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$ complex. (c) I.R.T.F spectrum of the gases evolved during the thermolysis of the $(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$ complex.

$(NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O$:

$$\begin{aligned} &\blacktriangleright (NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \cdot nH_2O \\ &\quad \rightarrow (NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 + nH_2O \\ &\blacktriangleright (NH_4)_3(Ta_{1-x}Nb_x)O(C_2O_4)_3 \rightarrow 1/2(Ta_{1-x}Nb_x)_2O_5 \\ &\quad + 3NH_3 + 3CO + 3CO_2 + 3/2H_2O \end{aligned}$$

3. Elaboration of tantalum carbide (TaC)

3.1. Carburization of the precursor by gas-solid reaction

In the preparation of tantalum and niobium carbide from a precursor elaborated by reaction of complexation, there is no need for the separation of the precursor from oxalates. Indeed, ammonium oxalate and oxalic acid are already decomposed at 300°C [26] because of their intrinsic physical characteristics. The carburization is carried out on the precursor in powder form under a flowing atmosphere composed of methane, source of carbon and hydrogen that acts as a reducer [27, 28].

As at high temperature, methane submits a thermal decomposition leading to pyrolytic carbon as shown in the equation below:

$$CH_4 \Leftrightarrow C + 2H_2. \qquad (3)$$

Hydrogen is introduced in the gaseous flow in order to displace the dissociation equilibrium.

For the gaz-solid reaction, this study takes into account several operating conditions such as the concentration of methane in the gaseous flow, the total flow rate, the heating rate, the final temperature of carburization, the duration of the isothermal treatment and the mass of sample [29].

The choice of every parameter is described in more details below.

The composition of the mixture is determined by two factors. Firstly, it is dependent on the carburization temperature. Indeed, according to Clar [27], the percentage of methane ranges from 1% to 3% when the synthesis temperature is included up to 1173 K.

Moreover, a lack of methane in the gaseous flow leads to a reduction process whereas a higher amount leads to the pyrolytic carbon contamination of the precursor. This latter isolates the solid particle from the reaction atmosphere and prevents the reaction from going on.

The total flow has to be sufficient for eliminating the gases evolved during the reaction away from the surface of the solid particles as acts the heating rate. Both allow a thorough exchange between the condensed and gaseous phases as they let the effluent gases issued from the complex decomposition to pass away from the solid.

The synthesis temperature is chosen to be up to 1173 K, the temperature that the reaction of carburization is thermodynamically possible.

The duration of the isothermal treatment takes into account the kinetic parameters of the reaction of carburization.

The mass of precursor submitted to the carburization process is determined by the characteristics of the gas-solid reaction in a horizontal bed reactor. In fact, in this kind of reaction, only the superficial layer of the horizontal bed of powder is in contact with the gases flow and can react.

On the other hand, the experimental apparatus such as the dimensions of the ceramic crucible, the diameter of the reactor or the length of the homogeneity thermal zone of the furnace act as limiting factors.

The conditions of the manufacturing procedure follow: a percentage of methane in the mixture of 1%, a gas mixture rate of 20 L/h, an isothermal temperature of 1273 K and a carburization time of 90 minutes.

The process consists of loading the precursor in the furnace, establishing the gaseous flow and starting the experiment thermal program.

When the reaction is finished, the reactor stays in the furnace in the same flowing mixture until it reaches the room temperature.

3.2. Characterization

The product is characterized by X-ray diffraction with a step scan of step size 0.02° at 4 s. The powder X-ray diffraction pattern of the sample is shown in Fig. 8.

The X-Ray diffraction pattern of the sample obtained after the carburization of the precursor shows the presence of tantalum carbide. The J.C.P.D.S file No 35-0801 of TaC with a cubic structure identifies the crystallographic phase [30].

The Table IV lists the reticular distances and their relative intensity on the diffraction pattern.

The carbide has been characterized by transmission electronic microscopy and it revealed an uniform surface showing aggregates of small crystallites. Their size range between 3.5 μm (Fig. 9a) and 150 nm (Fig. 9b).

TABLE IV Indexation of the diffraction pattern

2θ	d_{hkl}	I/I°
34.729	2.581	100
40.359	2.233	70
58.479	1.577	41
69.879	1.345	41
73.528	1.287	14
87.493	1.114	6
98.085	1.020	10
101.460	0.995	12
116.065	0.908	3

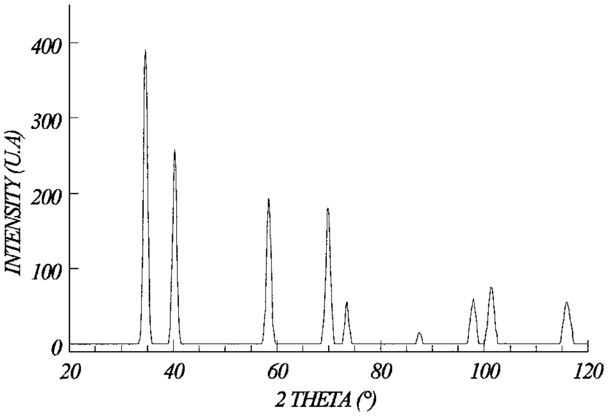
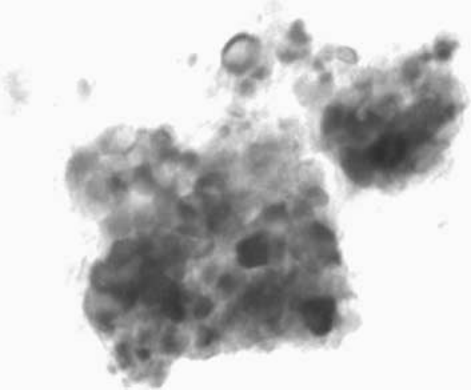


Figure 8 X-Ray diffraction pattern of TaC.



(a)

(b)

Figure 9 (a) Micrography of tantalum carbide grain powder. (b) Micrography of tantalum carbide grain powder.

4. Conclusion

The present laboratory-scale study indicates that the carburization by solid-gas reaction of an oxalic precursor from tantalite mineral yields to tantalum carbide at temperature lower than 1273 K. The chemical process allows eliminating the iron and manganese impurities. The reaction of complexation provides a mixed homogeneous precursor ready to be submitted to the carburization. The gas-solid reaction of this complex under flowing hydrogen-methane atmosphere lets to convert it in homogeneous tantalum-niobium carbide. The parameters of the reaction that must be controlled are the percentage of methane in the gaseous flow mixture, the total flow rate, the heating rate, the final temperature of carburization, the duration of the isothermal treatment and the mass of sample.

During the reaction, the oxalic complex is decomposed releasing water, ammonia, carbon monoxide and carbon dioxide. Our method of synthesis combines the advantages of the "chimie douce" process such as high reactivity of the precursor in fine powder form and those of the gas-solid reaction, which allows a good thorough exchange between the condensed and gaseous phase. The liquid phase processing has economical advantages over thre more conventionnal process. Further studies are being carried out to perform this technique and to generalize to other source of tantalum mineral, the production of TaC.

Acknowledgements

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