

# Effects of heating in air and chlorine atmosphere on the crystalline structure of pure Ta<sub>2</sub>O<sub>5</sub> or mixed with carbon

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Structure changes undergone by pure amorphous hydrated tantalum oxide mixed with different types of carbon when heated in air or chlorine atmospheres were monitored by X-ray diffraction (XRD) and scanning electronic microscopy (SEM). Heating in air of pure Ta<sub>2</sub>O<sub>5</sub> causes the appearance of the hexagonal structure δ-Ta<sub>2</sub>O<sub>5</sub> at 973 K and the orthorhombic structure β-Ta<sub>2</sub>O<sub>5</sub> at 1173 K. Heating in chlorine atmosphere markedly lowers the temperature at which transformation to the orthorhombic phase occurs. This effect is attributed to recrystallization of tantalum oxide from tantalum chloride and oxygen, both in gaseous phase, formed in a previous chlorination step of the amorphous oxide. When the thermal treatment is performed in chlorine atmosphere the presence of carbon permits the detection of the hexagonal form at 753 K; this temperature varies with the type of carbon and the oxide:carbon ration. © 1998 Kluwer Academic Publishers

## 1. Introduction

Tantalum oxides can be present in different crystalline structures. The existence of each structure depends on varied factors. Terao [1] studied by X-ray diffraction (XRD) the structural changes suffered by tantalum oxides when heated in oxygen and air and identified various forms of these oxides, among them an hexagonal structure δ-Ta<sub>2</sub>O<sub>5</sub> obtained at low temperatures when amorphous Ta<sub>2</sub>O<sub>5</sub> is heated in air. This hexagonal structure has also been found by Jeon *et al.*, when films of amorphous Ta<sub>2</sub>O<sub>5</sub> were treated at 1073 K [2]. Harvey and Wilman [3] investigated by electron diffraction (ED) the effect of heat on thin films of amorphous tantalum oxide and observed that a crystalline phase of hexagonal form occurs above 973 K and that further heating leads to an orthorhombic structure, β-Ta<sub>2</sub>O<sub>5</sub>.

Bansal [4] investigated by means of XRD, differential thermal analysis (DTA), thermogravimetric analysis (TGA) and infrared spectroscopy (i.r.) the phase transformations undergone by an amorphous Ta<sub>2</sub>O<sub>5</sub> gel under the effect of airheating. This author observed that the orthorhombic structure forms at 673 K with a short-range order, and that further heating to 1723 K leads to the tetragonal structure α-Ta<sub>2</sub>O<sub>5</sub>, the latter being a slow reversible process.

Ta(V) oxide occurs in two different stable forms: an orthorhombic structure β-Ta<sub>2</sub>O<sub>5</sub> and a tetragonal structure α-Ta<sub>2</sub>O<sub>5</sub>, for low and high temperatures,

respectively. The transition between these two forms takes place at 1633 K [5–7].

Amorphous hydrated Ta(V) oxide (Ta<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O) can be obtained by different procedures, such as TaCl<sub>5</sub> hydrolysis or fusion of oxides with KHSO<sub>4</sub> followed by hydrolysis. This hydrated oxide is insoluble in water and after being dried off it keeps approximately 8% of water, which is eliminated by heating at high temperatures [8,9].

The purpose of the present work was to examine by XRD and scanning electron microscopy (SEM) the formation of different low-temperature crystalline structures from amorphous hydrated Ta<sub>2</sub>O<sub>5</sub> heated in air and chlorine atmospheres and the effect of carbon when this oxide is heated in chlorine current.

## 2. Experimental procedure

### 2.1. Materials

The starting material was an amorphous hydrated tantalum oxide, of particle size between 5 and 100 μm, obtained by fusion of an orthorhombic Ta<sub>2</sub>O<sub>5</sub> (Fluka AG, CH-9470 Buchs) with KHSO<sub>4</sub>. The fusion was carried out in a Pt capsule and then an adequate volume of hot water was added to the fused material.

The gel was filtered and washed until complete elimination of potassium. The solid obtained was dried at 423 K to weight constancy and then analysed

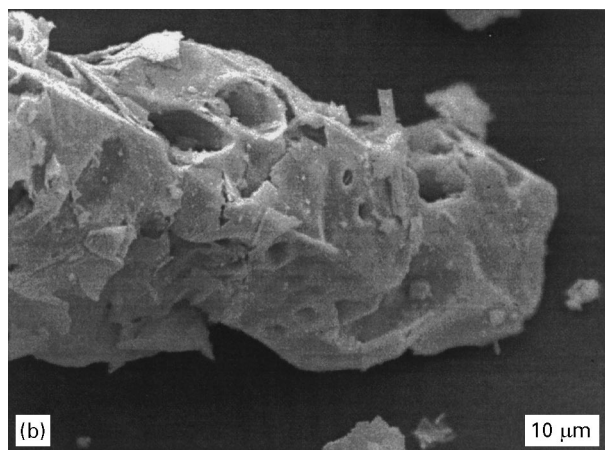
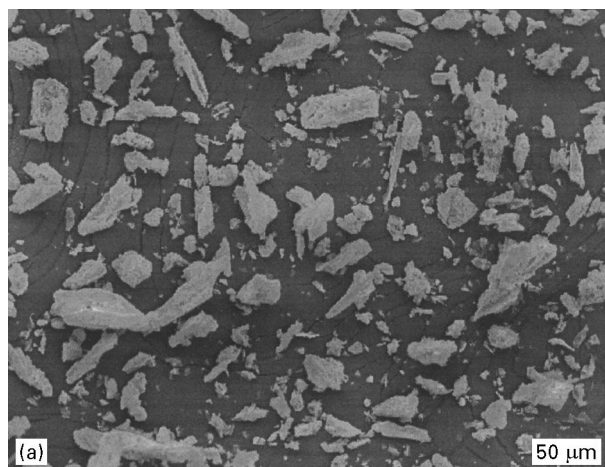


Figure 1 SEM micrographs of amorphous hydrated tantalum oxide particles. (a) Size of particles and (b) particle surface.

by XRD, SEM and i.r. Micrographs are shown in Fig. 1(a) and (b).

Fig. 1(a) shows the size of the amorphous oxide particles, with an irregular morphology and Fig. 1(b) shows the appearance of the particle surface.

The gases used in the hydrated oxide heating assays were air and chlorine (99.5%). Nitrogen (99.99%) was used as a purging gas. All the gases were conveniently dried before being put in the reaction zone.

Various mixtures were prepared, in different proportions, of hydrated tantalum oxide and three types of carbon (carbon blacks, provided by Cabot Corporation; graphite, of Fluka Chemie AG, CH-9470 Buchs; and a carbon prepared in our laboratory by heating sucrose, Fluka Chemie AG, CH-9470 Buchs, at 1273 K in inert atmosphere for 48 h. The specific surfaces of the carbons, determined by the Brunauer–Emmett–Teller (BET) method at 77 K with krypton adsorption, were 13.6, 9.7 and 0.6 m<sup>2</sup> g<sup>-1</sup> for carbon blacks, graphite and sucrose carbon, respectively.

## 2.2. Equipment

The equipment used for the amorphous oxide heating assays is shown in Fig. 2. The transformations undergone by the sample were monitored by XRD, with a Rigaku D-Max IIC diffractometer, operated at

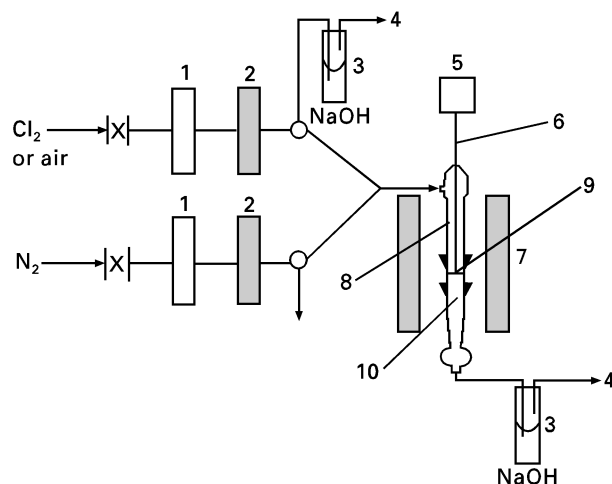


Figure 2 Diagram of the experimental equipment. 1. Drying unit; 2. flowmeters; 3. gas scrubbing trap; 4. exhaust; 5. digital thermometer; 6. thermocouple; 7. furnace; 8. gas preheater; 9. sample; 10. condenser.

35 kV and 30 mA by employing Ni-filtered and CuK<sub>α</sub> radiation,  $\lambda = 0.15418$  nm and by SEM with a Philips 515 microscope.

## 2.3. Procedure

The procedure used for the heating assays of pure amorphous oxide or mixed with carbon in different atmospheres was identical in all cases. After placing the sample in the reactor, a nitrogen stream was passed until the working temperature was reached. The nitrogen flow was then interrupted and air or chlorine were passed (50 cm<sup>3</sup> min<sup>-1</sup> at 1.013 × 10<sup>5</sup> Pa) for the time the experiment lasted. The system was purged with nitrogen after each assay. Sample heating and system purging times were standardized for all the runs.

The samples treated under different conditions were then analyzed by XRD and SEM.

## 3. Results and discussion

### 3.1. Amorphous Ta<sub>2</sub>O<sub>5</sub> · nH<sub>2</sub>O heated in air

The amorphous tantalum oxide samples heated in air current for 5 h underwent mass losses of 0.7, 1.98, 4.6 and 5.9% at 873, 973, 1073 and 1173 K, respectively.

Fig. 3 shows the X-ray diffraction patterns of the treated solids. It can be observed that at 873 K there is an ordering of the oxide structure, and that the crystalline structure of the sample heated at 1173 K somewhat different from those of the samples treated at 973 and 1073 K.

Fig. 4 shows the diffraction patterns of the hexagonal and orthorhombic structures of tantalum oxide obtained by simulation from the corresponding JCPDS files. It can be noted that both structures exhibit similar distribution of the highest peaks. However, in the orthorhombic structure peaks split up into doublets at  $2\theta = 28.5; 37; 50.5; 55.5$  and 59.

From a comparative analysis of Figs. 3 and 4, it can be inferred that air-heated amorphous hydrated

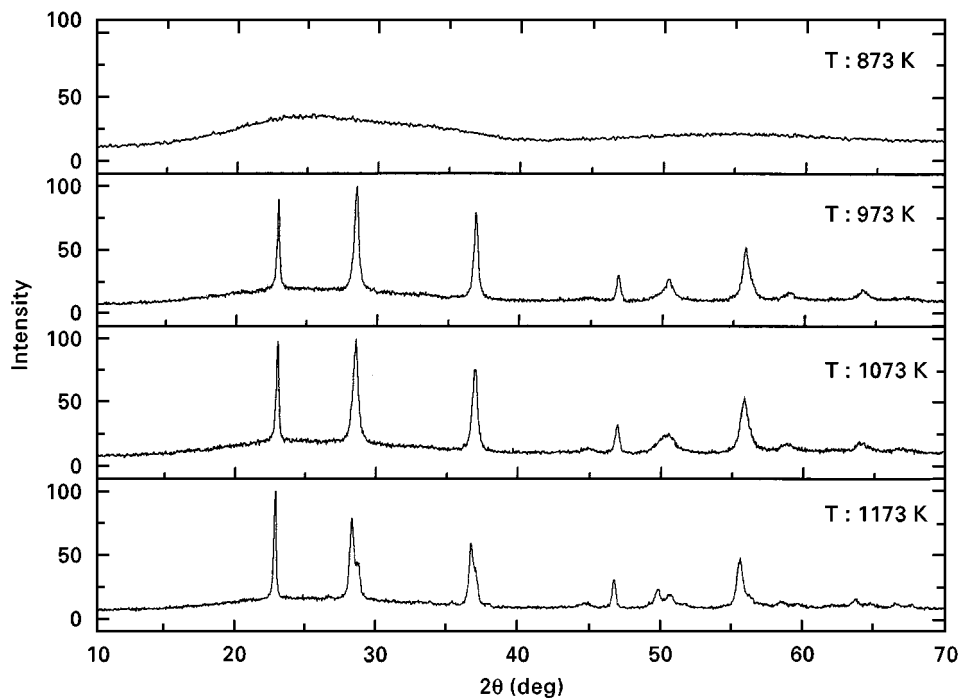


Figure 3 X-ray diffraction patterns of products obtained by heating in air of amorphous  $Ta_2O_5 \cdot nH_2O$ .

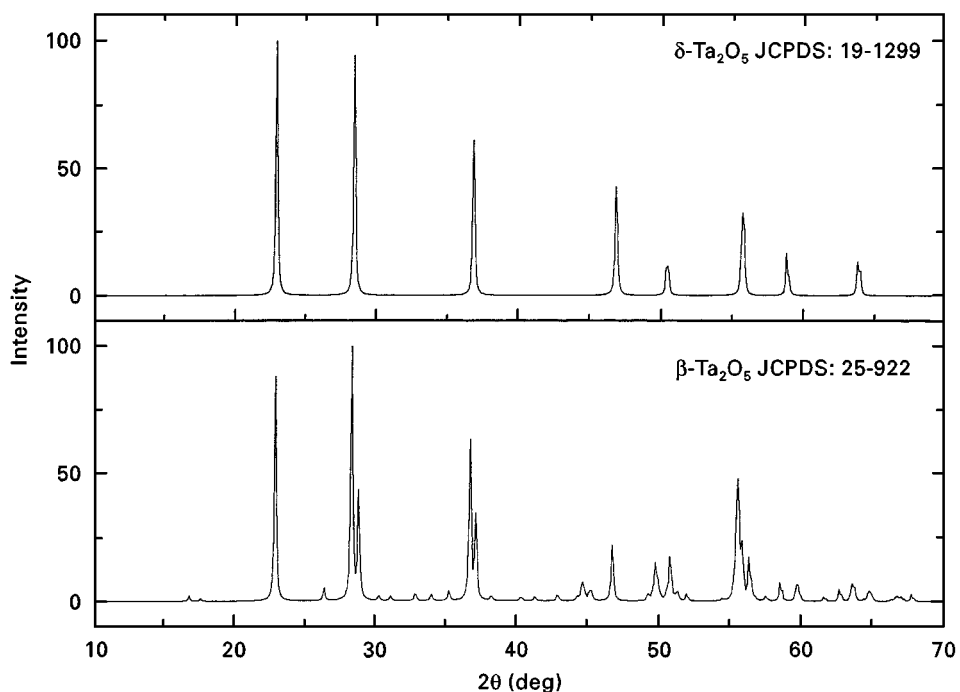


Figure 4 X-ray diffraction patterns of hexagonal,  $\delta-Ta_2O_5$ , and orthorhombic,  $\beta-Ta_2O_5$ , structures of tantalum oxide.

tantalum oxide crystallizes into different structures according to the heating temperature. In the first heating stage, an hexagonal structure is obtained which becomes into an orthorhombic phase when the samples reaches 1173 K. These results are in agreement with the literature reported values for the effect of thermal treatment on thin films of amorphous tantalum oxide [2, 3].

The results obtained by DTA (performed in inert atmosphere on a DTA 50 Shimadzu) of the amorphous oxide showed two exothermic zones. The first one

lies between 873 and 1073 K and the second one starts at 1123 K. These temperatures match those at which structure changes were observed. This might indicate that the mass losses, caused by dehydration of tantalum oxide, are associated to the structure changes undergone by the sample at the different stages of the thermal treatment.

The i.r. spectrum (obtained on a Bruker IFS 25) performed on the untreated amorphous tantalum oxide showed the presence of water but not of the hydroxyl group. Therefore the dehydration of the sample

at the different heating stages is probably caused by the loss of the hydration water contained in the original sample.

Fig. 5(a) and (b) shows that no morphological or surface changes have taken place after thermal treatment.

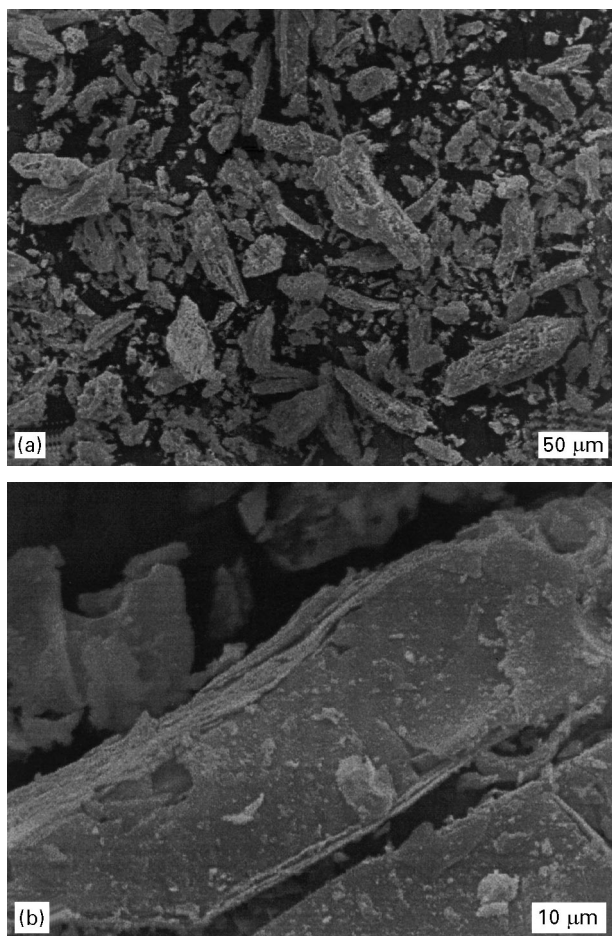


Figure 5 SEM micrographs of starting oxide particles after air treatment at 1173 K, for 5 h.

### 3.2. Amorphous $Ta_2O_5 \cdot nH_2O$ heated in chlorine atmosphere

Fig. 6 shows the X-ray diffraction patterns of the samples heated in chlorine atmosphere, at different temperatures, for an hour. It can be observed that tantalum oxide starts to crystallize into the orthorhombic form at 873 K, while in air this structure is only formed after the sample has been heated at 1173 K for 5 h.

These results might indicate that the structure change does not occur by effect of the heating but as a consequence of the gaseous phase reaction between tantalum chloride and oxygen formed in a previous stage of oxide chlorination. This is in agreement with results obtained in previous studies of the accelerating effect of chlorine on the phase transformation of  $ZrO_2$  [10] and  $TiO_2$  [11] oxides and transition aluminas [12].

Fig. 7 shows the micrographs of the samples subjected to the action of temperature in chlorine atmosphere. Fig. 7(a) shows the effects of chlorine by the attack on particle surface. The growth of microcrystals on the surface of the starting oxide can be observed in Fig. 7(b) and (c).

The reaction between  $Ta_2O_5$  and  $Cl_2$  is not thermodynamically favourable. The equilibrium vapour pressures are of 137, 0.2, 103 Pa and 101 kPa for  $TaOCl_3$ ,  $TaCl_5$ ,  $O_2$  and  $Cl_2$ , respectively [13]. The vapour pressure values of the Ta chlorides and oxygen, though low, are apparently enough to allow the formation of the observed new crystalline structure. This has already been noted by other authors working with similar systems [10–12].

The mass losses detected in chlorine were 0.6, 2.47, 5.53 and 15.8% for treatments at 823, 873, 973 and 1173 K, respectively. These mass losses, besides being associated to the sample dehydration, as in the previous case, are a result of the volatilization of some of

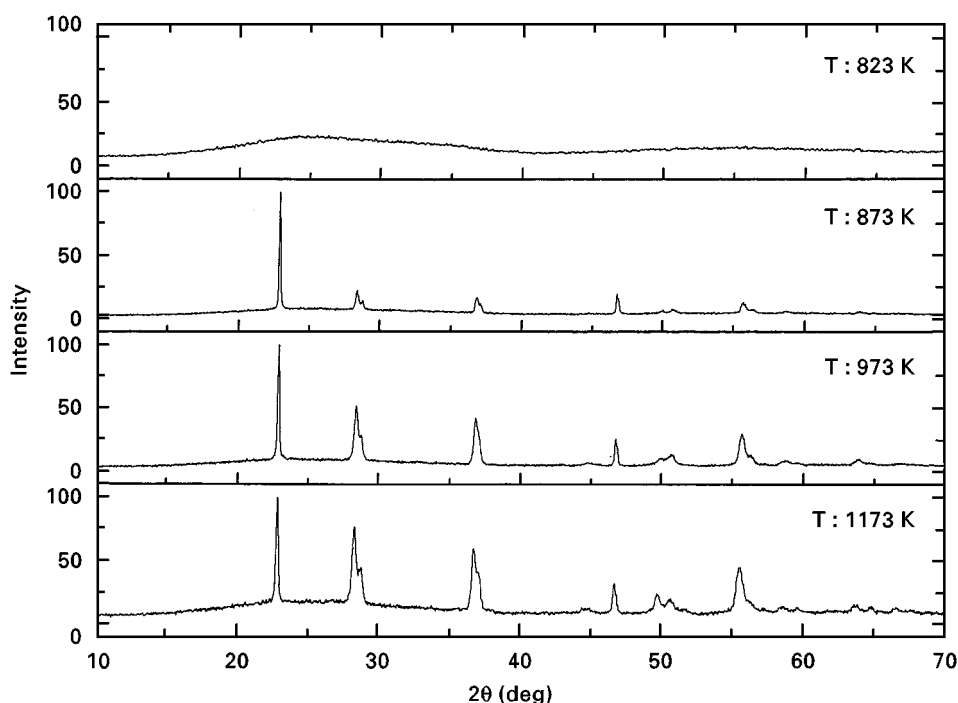


Figure 6 X-ray diffraction patterns of products obtained by heating in chlorine atmosphere of amorphous  $Ta_2O_5 \cdot nH_2O$ .

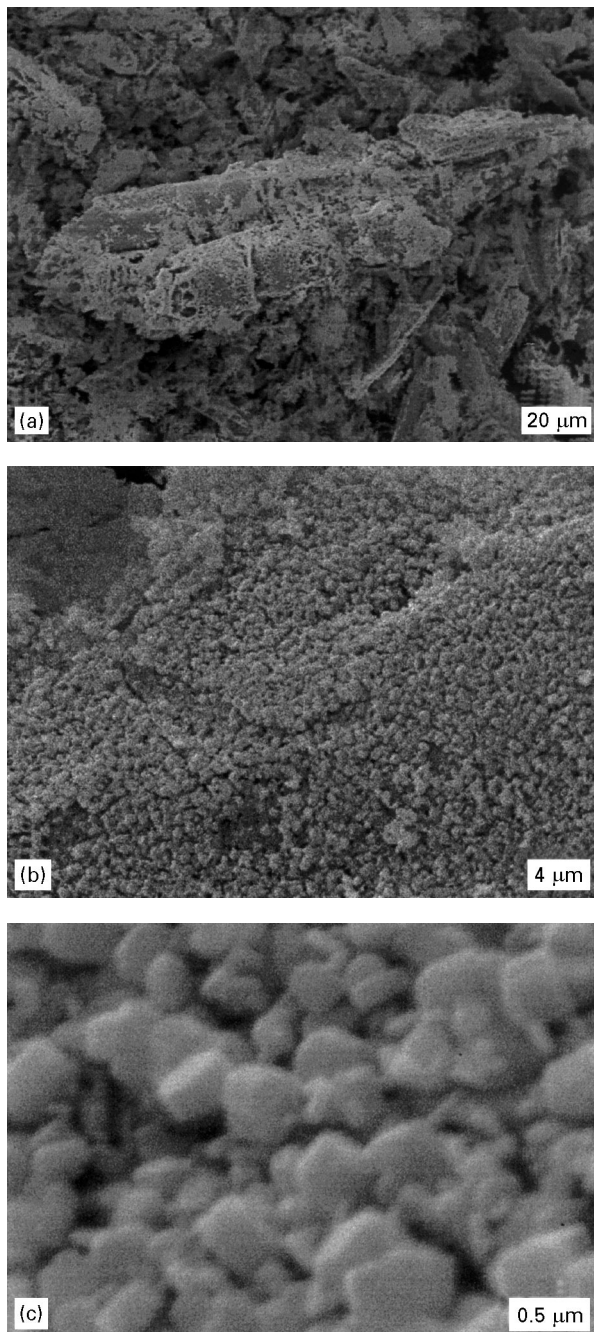


Figure 7 SEM micrographs of starting oxide particles after treatment in chlorine atmosphere at 973 K, for 1 h.

the tantalum chloride formed during oxide chlorination, which is thermodynamically favoured by the temperature increase.

### 3.3. Amorphous $Ta_2O_5 \cdot nH_2O$ mixed with three different types of carbon and heated in chlorine atmosphere

Heating assays in chlorine atmosphere were performing using the amorphous oxide mixed with different types of carbon. The mixtures contained carbon proportions such that carbon surface areas were equivalent in each case.

The X-ray diffraction patterns of the oxide mixed with different amounts of sucrose carbon and sub-

jected to the action of temperature in chlorine atmosphere for one hour are shown in Fig. 8.

From Figs. 6 and 8, it can be observed that the temperature of crystallization into the above mentioned forms is decreased by the presence of carbon, as compared with results obtained by heating in chlorine atmosphere without carbon. At carbon concentrations of 50%, the hexagonal phase was detected at 753 K, while there were no structure changes at carbon concentrations of 10%.

From Fig. 8 it can be also inferred that, with fixed oxide-carbon proportion and increasing temperature, the structure changes are similar to those observed in air and chlorine treatments.

Fig. 9(a) and (b) shows the formation of crystals in hexagonal phase, which shows different habit from that observed for orthorhombic phase in Fig. 7(c).

The results obtained by other researches when studying the decomposition of chlorine on carbon surface [14–16] can account for the results obtained here. Active chlorinating species, such as atomic chlorine or free radicals, are formed on the carbon surface. These accelerate the oxide chlorination reaction causing higher tantalum chlorides and oxygen concentrations in the gaseous phase which in turn generates the new crystalline phase of the oxide.

Furthermore, the heating in nitrogen of the oxide mixed with carbon was assayed in order to determine the impact of carbon on the observed transformations. The results matched those obtained for air heating of pure amorphous oxide.

The mass losses undergone by the sample are reported in Table I. These are due to the same causes as those discussed for the treatment with chlorine. A higher volatilization of tantalum chloride was observed, which was expected as carbon favours the chlorination reaction both by catalysing the formation of active species and thermodynamically because it is a reducing agent capable of combining with the oxygen released during such reaction.

Fig. 10 shows the results obtained in the treatment of mixtures of amorphous oxide with the three studied carbons (equivalent surface areas) at 753 K. Structure changes occurred only when sucrose carbon was used, indicating that this carbon is more reactive than the other two. The XRD pattern for the oxide-graphite mixture is the same as that for pure graphite.

Carbon black-oxide mixtures proved to be more reactive than graphite-oxide mixtures, as can be seen from the order of reactivity of these two mixtures with equivalent carbon surface areas shown in Fig. 11.

The results obtained when the amorphous tantalum oxide was mixed with carbon and heated in chlorine atmosphere can be explained by taking into account the fact that each carbon has different surface functional groups. Therefore, when chlorine decomposes on the carbon surface different activated chlorinating species are formed in varying proportions [14–16]. Consequently, the chlorinating reaction that generates the gaseous compounds from which the new crystalline structures are formed can be enhanced to different degrees.

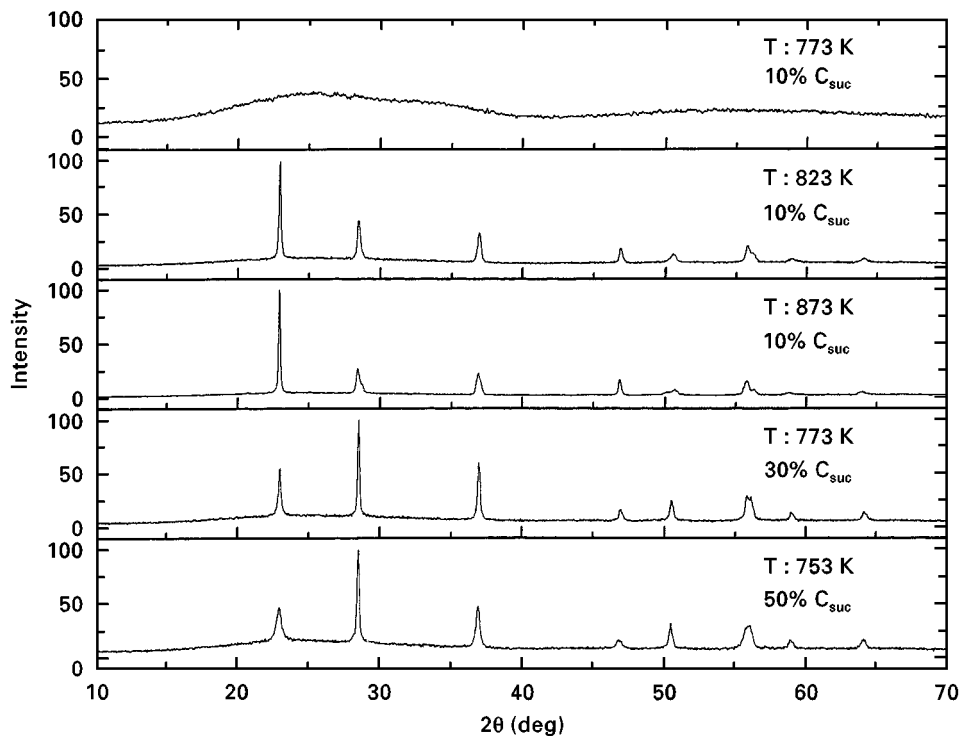


Figure 8 X-ray diffraction patterns of products obtained by heating in chlorine atmosphere of amorphous  $Ta_2O_5 \cdot nH_2O$  mixed with sucrose carbon.

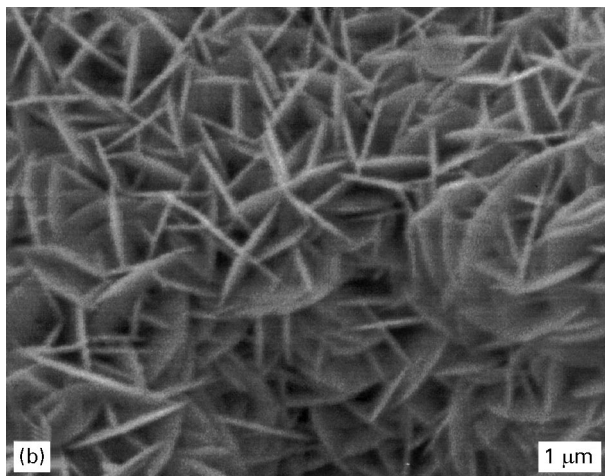
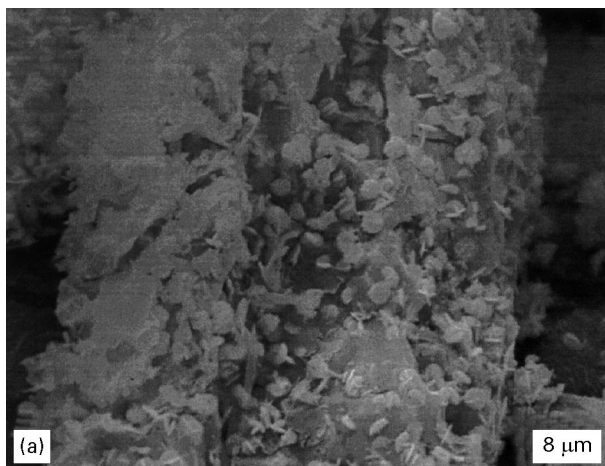


Figure 9 SEM micrographs of particles of starting oxide mixed with carbon sucrose after treatment in chlorine atmosphere.

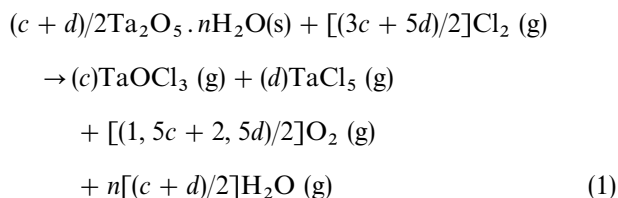
TABLE I Mass losses undergone by tantalum oxide mixed with sucrose carbon when heated in chlorine

Temperature (K)	Carbon concentration (wt %)	Mass loss (wt %)
773	10	0.1
823	10	3.1
873	10	45.9
773	30	3.1
853	50	3

The experimental data shown in Figs 10 and 11 permit us to state that from the three studied carbons, sucrose carbon is the most reactive one, followed by carbon black. In the former, a smaller carbon surface is required for the structural change to occur at 753 K.

#### 4. Conclusions

The thermal treatment in chlorine atmosphere of amorphous hydrated tantalum oxide leads to the formation of the orthorhombic structure of this oxide at temperatures lower than those required for this transformation to occur in air atmosphere. The following reaction scheme can be proposed for this process



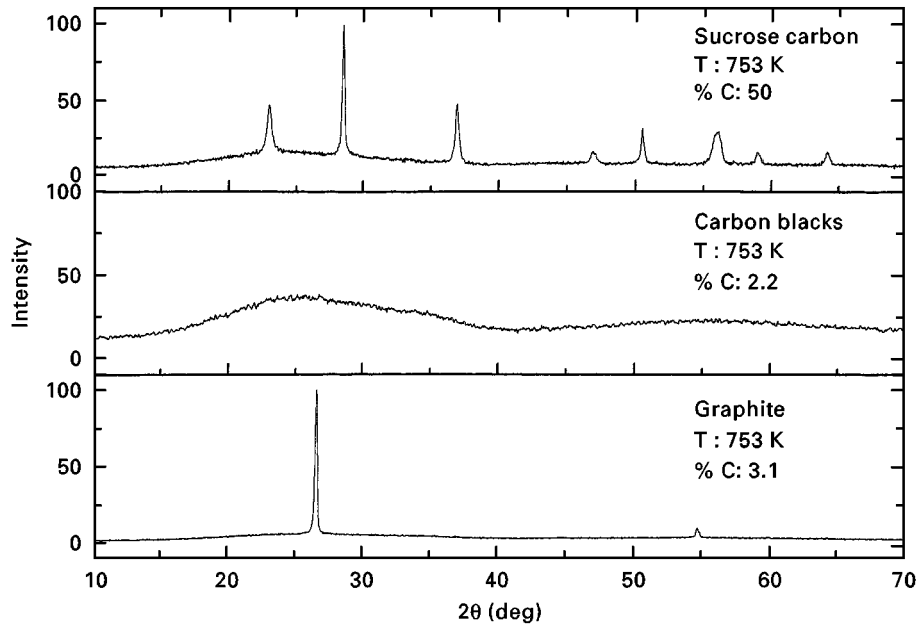


Figure 10 X-ray diffraction patterns of products obtained by heating in chlorine atmosphere of amorphous  $Ta_2O_5 \cdot nH_2O$  mixed with different types of carbons and equivalent surface areas.

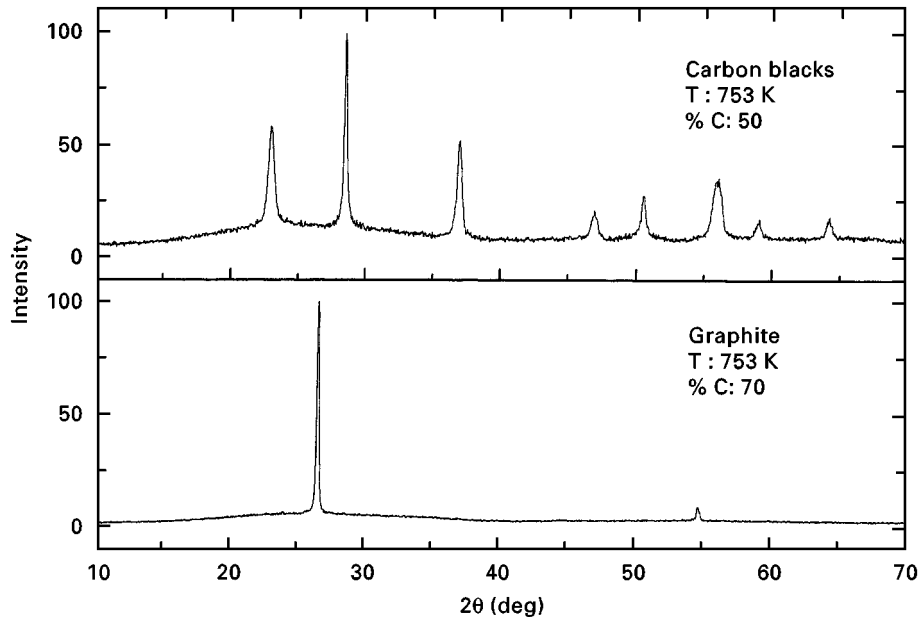
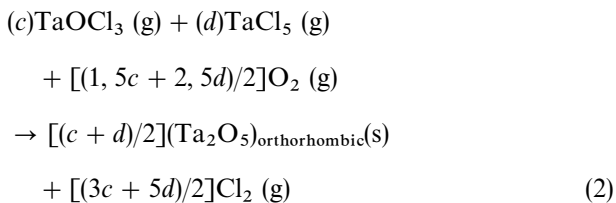


Figure 11 X-ray diffraction patterns of products obtained by heating in chlorine atmosphere of amorphous  $Ta_2O_5 \cdot nH_2O$  mixed with carbon black and graphite (with equivalent surface areas).

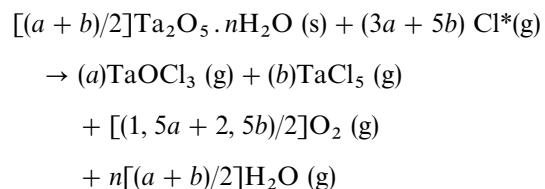
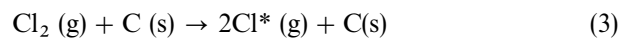


Link:  $c + d = 1$ , where  $c$  and  $d$  can vary between 0 and 1.

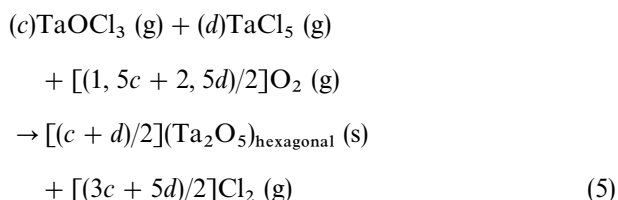
When the amorphous oxide is heated in chlorine atmosphere, the presence and nature of carbon have a marked effect in the occurrence of the hexagonal crystalline structure. This effect could be attributed to the formation of active chlorinating species on the carbon surface. These species favour the oxide chlorination reaction with the subsequent increase of the tantalum

chloride and oxygen concentrations, both in gaseous phase, from which new crystals are formed.

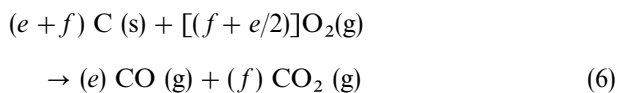
The formation of active chlorinating species might prevail on carbon oxidation, enabling the oxygen partial pressure in the gaseous phase to be high enough to make the reaction of amorphous tantalum chlorination reversible. The following reaction scheme can be proposed



Link:  $a + b = 1$ , where  $a$  and  $b$  can vary between 0 and 1.



Link:  $c + d = 1$ , where  $e$  and  $f$  can vary between 0 and 1.



Link:  $e + f = 1$ , where  $e$  and  $f$  can vary between 0 and 1.

Where Reaction 5 might prevail over Reaction 6, when  $\text{Cl}_4$  formation of active chlorinating species prevails on carbon oxidation.

The studied carbons can favour structure changes of amorphous tantalum oxide to different degrees. This is shown by the following reactivity per surface area unit ordering: sucrose carbon > carbon blacks > graphite.

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