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Formation of NbC and TaC from Gel-Derived Precursors

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Abstract

Binary hydrogels, in which a niobium or tantalum oxide gel and a pyrolysable organic compound are combined, were prepared as preceramic materials. Carbonaceous gel or saccharose is used as the organic gel constituent, and alkoxides or peroxo acids are the starting materials for the transition metal component. Under pyrolysis at 600–700°C, the gels are transformed into carbide precursors in which a reactive carbon and finely dispersed oxide particles are mixed intimately. The subsequent carbothermal reduction proceeds at lower temperatures compared to physical mixtures of oxides and carbon black. The high-temperature treatment was monitored by TG/DTA, X-ray diffraction and nitrogen adsorption. Microporosity is generated in the temperature range 700–800°C, and mesoporosity is additionally formed at higher temperatures. The changes in porosity are controlled by the processes of crystallization, carbothermal reduction and sintering. The final products at 1400–1500°C are assemblages of fine particles of the face-centred cubic carbides with grain sizes of 1 μm and less. © 1997 Elsevier Science Limited.

1 Introduction

Carbides and nitrides of the transition metals of the fourth to sixth groups of the periodic table possess high melting points, high hardness and excellent high-temperature strength. Therefore they are frequently referred to as refractory materials and find application as cutting tools, wear-resistant parts and high-temperature structural materials. Polycrystalline carbides needed for these applications are conventionally prepared by solid-state reactions of metal or metal oxide powders with carbon leading to materials of a low specific surface area. In addition to the classical refractory properties, the transition metal carbides are being used increasingly for their electrical conductivity and chemical corrosion resistance as electrodes, catalysts, conducting films or oxidation-resistant coatings; however, usage in catalysis and electrochemistry requires materials of high surface areas.

Interest in the electrical, catalytical and anticorrosion properties has necessitated the development of new preparation techniques. Various vapour deposition techniques have been developed for the coating of substrates, especially of steel, with carbides and nitrides.[1,2] The oxidation resistance of TaC is also used in multilayer coating systems for the protection of carbon materials.[3] Electrochemically prepared precursors for TaC coatings on various substrates have been described previously.[4] The temperature-programmed reaction method of Oyama and Boudart and their co-workers overcomes the problems of low surface areas.[5,6] It consists of carburizing an oxide in a CH_4/H_2 atmosphere and leads to specific surface areas of 100–200 m^2/g for WC and Mo_2C. For NbC and TaC, however, the surface areas never exceeded 11 m^2/g. The decomposition of layered niobium acids intercalated by amines appears to be an original technique for the production of porous NbC at a low temperature of about 1000°C.[7] But carbide formation needs polyacronitrile as an additional carbon source, and it is supposed that porosity is mainly associated with residual carbon (up to 50%). Transesterification of transition metal alkoxides has been found useful in synthesizing polymeric precursors which can be converted to fine carbide powders at temperatures lower than those necessary with conventional solid-state reactions.[8]

As an alternative to these techniques, we have investigated carbide formation from binary gel

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precursors composed of a metal oxide and a pyrolysable carbon compound. This sol–gel route comprises (1) mixing of a sol of a metal oxide hydrate and a sol or solution of the carbon compound, (2) transformation of the binary sol into a homogeneous gel if at least one of the constituents is a gel former, (3) thermal conversion of the gel into a precursor consisting of colloidal oxide particles dispersed in a carbon matrix and (4) carbothermal formation of the carbide. The advantages are an improved kinetics in the carbothermal reduction reaction and the formation of characteristic textures, e.g. materials with intercrystalline porosity or fine particles with high external surface areas.

In this work, the metal oxide gel constituent is prepared either by hydrolysis of the correspondent alkoxide or by using peroxo niobium acid or its tantalum version. These peroxo acids may be easily formed by dissolving the freshly prepared hydroxides in hydrogen peroxide. These solutions proved very useful for the preparation of mixed gels because they convert by thermal decomposition of residual H_2O_2 into sols and gels.

The alkoxide technique is a traditional method in the silica and metal oxide sol–gel chemistry for the production of glasses and oxide ceramics. Moreover, it is also applicable to very pure non-oxide ceramic systems. Disadvantages, however, are the inaccessibility and expense of the metal alkoxides. Recently, the alkoxide technique has been used for the preparation of binary inorganic–organic gels and their carbothermal conversion to SiC[9] and ZrC.[10] Because transition metal alkoxides react faster with water than silicon alkoxides, their sols have to be stabilized with complexing agents against precipitation.

Starting from various metal oxide sols and carbon precursors, a variety of compositions and textures of materials may be achieved. This paper deals with binary systems derived from metal alkoxides or peroxo acids, containing carbonaceous sol or saccharose as the carbon source, and their thermal treatment. The carbonaceous sol was prepared by chemical modification of a coal tar pitch.[11] It has been found that the carbonaceous sol, having sulphonic and carboxylic groups, changes reversibly in aqueous and alcoholic media between sol and gel, and pyrolyses into almost pure carbon.[12] In the binary gels, the reaction sequence during the carbothermal reactions are followed by TG/DTA, X-ray diffraction and nitrogen adsorption. The thermal behaviour of physical mixtures of Nb_2O_5/carbon black and Ta_2O_5/carbon black have been investigated for comparative studies.

2 Experimental Procedure

2.1 Sample preparation

2.1.1 Niobium peroxide sol and gel

Free peroxo niobium and tantalum acids are known to be prepared by adding sulphuric acid to the corresponding peroxo niobates or tantalates.[13] Under these acidic conditions, however, condensed peroxo acids, mostly insoluble in water, are formed. In order to obtain peroxo acids in aqueous solution, a preparation technique under neutral conditions, the dissolution of hydroxides in H_2O_2, was used here.

Niobium hydroxide was precipitated from a solution of 2·70 g $NbCl_5$ (0·01 mol) (E. Merck) in dilute HCl using liquor ammonia. The hydroxide was washed with water by decantation and then by filtration until no Cl^- ions could be detected in the filtrate. This freshly prepared hydroxide was suspended in 5 ml distilled water at 0°C and treated with 10 ml 15% H_2O_2 under stirring. After about 1 h, a transparent yellow, acidic solution of pH = 1–2 resulted, showing that a peroxo niobic acid had formed. Excess of H_2O_2 and ~50% of the water were removed by subsequent heating at 80°C, yielding a yellow peroxide sol free of insoluble particles. During this heating process the sol became neutral. The peroxide sol turned into a gel after storage for several days. For the production of binary gels, however, a second solution containing a pyrolysable organic compound was added before the peroxide solution gelled.

2.1.2 Niobium peroxide/saccharose gel

An aqueous solution of saccharose was added to the peroxide sol with a weight ratio 1·35 g saccharose/0·01 mol Nb at room temperature. The amount of saccharose has been chosen to adjust the stoichiometric ratio C/Nb_2O_5 to 7 in the pyrolysed (600°C) xerogel. Upon heating at 80°C, the solvent (water) was partially evaporated until the viscosity of the sol strongly increased. This viscous sol turned into a gel under cooling. The remaining water was allowed to evaporate first at room temperature and thereafter at 110°C. Thus, a yellow non-crystalline mixed xerogel was obtained.

2.1.3 Niobium alkoxide/carbonaceous gel

An alkoxide-derived niobium pentoxide sol was prepared by adding 3 ml 30% H_2O_2 dropwise to methanol-diluted $Nb(OC_2H_5)_5$ (0·01 mol $Nb(OC_2H_5)_5$ + 12 ml methanol) at 0°C. Subsequent heating of the sol up to 40°C led to a clear yellow solution. The carbonaceous sol was prepared by dissolving 0·58 g of dried carbonaceous gel in a mixture of 5 ml 3% H_2O_2, 6 ml ethanol and 0·58 g glycerol.

The carbonaceous gel was obtained from a coal tar pitch;[11] it had an elemental composition of 62·0 wt% C; 2·8 wt% H; 0·7 wt% N; 6·2 wt% S; and 28·3 wt% O. The alkoxide-derived sol and the carbonaceous sol were mixed at room temperature under stirring. The binary sol was then transformed into a binary gel on a hot plate at 60°C. Excess of solvents was removed first at 60°C and then at 110°C, leading to fragments of a xerogel.

2.1.4 Tantalum peroxide sol and gel

Tantalum hydroxide was precipitated from a solution of 3·58 g $TaCl_5$ (0·01 mol) (E. Merck) in dilute HCl using liquor ammonia. After the freshly prepared hydroxide had been washed carefully (free of Cl^-), it was dissolved in 40 ml 15% H_2O_2 under stirring (~1 h) at room temperature. The solution of the peroxo acid thus formed was colourless and acidic. Excess of H_2O_2 and ~50% of the water were then removed by heating at 80°C, leading to an almost neutral sol. A peroxide gel could be obtained from this sol by further heating at 80°C. Drying at 110°C gave the xerogel which was investigated by TG/DTA.

2.1.5 Tantalum peroxide/saccharose gel

Saccharose 1·35 g, diluted in 2 ml distilled water, was added to the sol containing 0·01 mol Ta. Under heating at 80°C, the mixed sol was concentrated until a colourless gel had formed. The xerogel was obtained by drying at room temperature and thereafter at 110°C.

2.1.6 Tantalum alkoxide/carbonaceous gel

A quantity of 4·06 g (0·01 mol) $Ta(OC_2H_5)_5$ (Fluka Co.) was dissolved in a mixture of 10 ml methanol and 5 ml acetylacetone (acetylacetone was used for stabilizing $Ta(OC_2H_5)_5$ against fast hydrolysis and precipitation). Then 0·37 g of the dried carbonaceous gel, dissolved in a mixture of 5 ml 3% H_2O_2, 10 ml ethanol and 0·37 g glycerol under heating, was mixed with the stabilized alkoxide solution. The mixed batch was then concentrated up to about 15 ml on a hot plate at 60°C under stirring. This resulted in a gel. Subsequent drying led to the xerogel.

2.1.7 Nb_2O_5/ and Ta_2O_5/carbon black mixtures

Acetylene black was mixed with monoclinic Nb_2O_5 and orthorhombic Ta_2O_5, respectively (both from E. Merck), in amounts according to a molar ratio $C/M_2O_5 = 7$. The mixtures were homogenized by dry milling in a ball mill for 6 h.

2.1.8 Heat treatment

The xerogels and powder mixtures were annealed in graphite boats using an alumina tube furnace (Carbolite Furnace Limited) at 600–1500°C at 100°C intervals in flowing argon. The heating rate was 10 K/min, and the holding time at the reaction temperature was 1 h.

2.2 Characterization

The thermal behaviour of the xerogels and the powder mixtures in argon atmosphere was studied by simultaneous TG/DTA using a SETARAM TAG 24 thermoanalyser. In addition, TGA was conducted in air for some final heating products, to study the oxidation behaviour of the carbides. The heating rate was 15°C/min in all cases.

Standard X-ray diffraction (XRD) with nickel-filtered CuK_α radiation was used to determine the crystalline phases present in the heat-treated samples.

Measurements of nitrogen adsorption/desorption areas (multipoint method) at 77 K were performed after drying and degassing the samples under vacuum for 3 h at 350°C using an ASAP 2000 instrument from Micromeritics, USA. BET surface areas, and pore volumesa $V_{1\text{-}100}$ for the range of pore radii 1–100 nm (this range comprises the mesopores and the narrowest macropores) as well as pore volume distributions using the BJH standard computational procedure, and t-plots (micropore surface areas and volumes) according to Harkins and Jura were calculated from the nitrogen isotherms.

Chemical analyses of the non-metals were performed with LECO TC-436 (for O and N) and with LECO CS-444 for carbon. Niobium and tantalum values were determined with a combustion technique at 1000°C in air in which the residual oxides Nb_2O_5 and Ta_2O_5 were weighed.

3 Results

Poreless amorphous xerogels have been formed upon drying at 110°C for all gel systems. Subsequent thermal processing up to 700°C in an inert atmosphere then includes calcination of the oxide hydrates and conversion of the organic materials into almost pure carbon. Chemical analyses at this pyrolysis stage give a C/M_2O_5 ratio for all systems close to 7, which fits the overall carbothermal reduction reactions.

3.1 The niobium systems

Simultaneous TG/DTA curves of the *Nb_2O_5/carbon black mixture* in the temperature range 20–1600°C (Fig. 1) show that mass is constant up to about 1100°C. Above this temperature, mass loss is observed in two endothermic steps centred at about 1130 and 1340°C. X-ray patterns of the mixture annealed at different temperatures show that monoclinic Nb_2O_5 is the only crystalline phase present up to 1000°C. At 1100°C, the lines of Nb_2O_5 and tetragonal NbO_2 can be simultaneously observed, indicating that the first mass loss step in the TG trace is due to the reaction

$$Nb_2O_5 + C \rightarrow 2\ NbO_2 + CO \qquad (1)$$

The conversion of NbO_2 into NbC according to

$$NbO_2 + 3\ C \rightarrow NbC + 2\ CO \qquad (2)$$

appears to begin at ~1200°C; the mixture reveals weak lines of the face-centred cubic carbide beside those of NbO_2. Further temperature increase lowers the intensity of the NbO_2 lines and strengthens those of NbC; at 1400°C only NbC is present.

TG/DTA curves of the *peroxide/saccharose gel* are depicted in Fig. 2(A). A peroxide gel without saccharose was additionally investigated (Fig. 2(B)) for comparison with the binary gel. The TG trace of the binary gel may be roughly divided in three sections. The first section ranging up to about 600°C is characterized by a substantial mass loss attributable to the pyrolysis of saccharose and the decomposition of the peroxide. The exothermic DTA peak at 190°C may be associated with the decomposition of the peroxide. The decomposition of niobium peroxide is reported in the literature[14] to occur at about 190°C. The second TG section (600–800°C) is that of a nearly constant mass. Above 800°C, however, the loss reflects the onset of the carbothermal reduction which runs over a broad temperature range.The TG steps centred at about 900, 1050 and 1380°C correspond to more or less separated endothermic peaks.

The TG/DTA curves in Fig. 2(B) show that the *niobium peroxide gel* decomposes in several steps. Three strong exothermic peaks are observed with their maxima at 190, 350 and 540°C. The peak at 190°C reflects the decomposition of the peroxide.[14] The corresponding mass loss may be associated with the release of oxygen and water. According to X-ray diffraction, the DTA peak at 540°C originates from the crystallization of Nb_2O_5 (no analogous peak is observable in the binary gel). Since the TG curve at this temperature reveals a mass loss before reaching a constant range, it is to be assumed that the release of residual water parallels the crystallization process. The DTA peak at 350°C may be caused by structural reorganizations in the amorphous gel network; however, they are not yet understood.

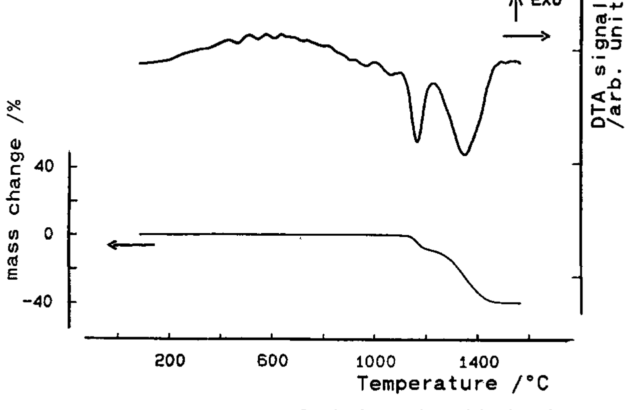


Fig. 1. TG/DTA diagram of Nb_2O_5/carbon black mixture.

The thermoanalytical curves of the *alkoxide/carbonaceous gel* (Fig. 3) reveal a mass loss of about 20% up to 600°C, proceeding in several overlapping endothermic steps. The first step begins almost upon heating at 100°C and may be associated with the loss of entrapped water and

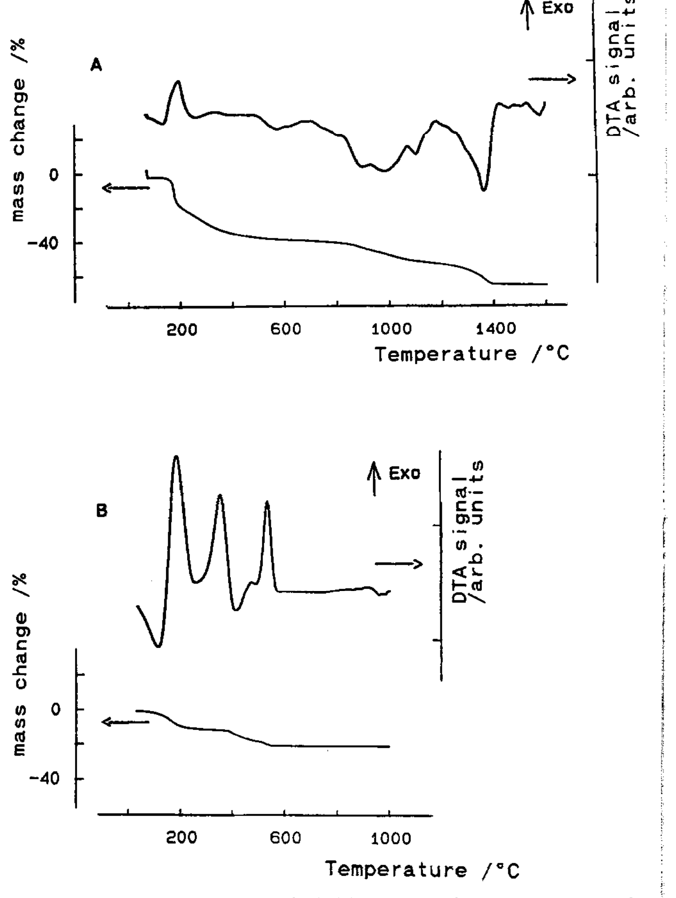


Fig. 2. TG/DTA diagrams of niobium peroxide/saccharose gel (A) and niobium peroxide gel (B).

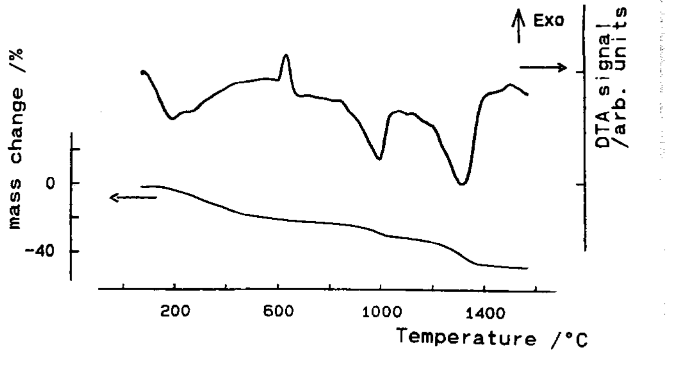


Fig. 3. TG/DTA diagram of niobium alkoxide/carbonaceous gel.

organic solvents. The second step is caused by the destruction of the functional groups of the carbonaceous gel, as found recently.[12] The pyrolysis of the carbonaceous gel and the loss of water and organic ligands strongly fixed to the alkoxide hydrolysis product lead to a mass loss tailing up to about 450°C. The temperature range 600– 800°C is characterized by a low mass loss (~3%). The DTA curve, however, reveals an exothermic peak at 640°C accompanied by a weak mass loss (not seen in Fig. 3), which is due to crystallization of Nb_2O_5 confirmed by X-ray diffraction (see later). This mass loss resembles the TG step found for the crystallization phenomenon of the peroxide and may be associated with loss of residual water. Above 800°C, mass decreases again through two different stages, indicating that the carbothermal reduction proceeds in at least two reaction steps. Both a sharp mass loss step centred at about 1030°C, and a broad mass loss at 1200–1400°C are accompanied by endothermal DTA peaks.

X-ray diffraction showed that the alkoxide/carbonaceous gel remains amorphous up to 600°C, and the peroxide/saccharose gel is amorphous up to 700°C. At 700 and 800°C, respectively, diffuse lines of orthorhombic Nb_2O_5 are observable, indicating that the amorphous oxide has crystallized and forms crystallites of nanometer size. Figure 4 depicts the patterns of the annealed alkoxide/carbonaceous gel; those of the peroxide/saccharose gel are nearly correspondent for temperatures above 700°C. The crystallization temperature of Nb_2O_5 in the binary gels is higher than in the peroxide gel without any carbonaceous admixture. The binary gels treated at 800°C also give some weak lines of the tetragonal form of NbO_2 in addition to those of Nb_2O_5. At 900°C, only NbO_2 is present. The X-ray patterns show that at this temperature the first reduction reaction is finished and is immediately followed by a second step leading to an f.c.c. carbide structure (the formation of an oxycarbide at this temperature is likely but could not be evidenced). A separation of both processes is perceptible only for the peroxide/saccharose gel in the DTA and TG curves. The mass loss from the end of the pyrolysis stage at 700°C to the end of the first reduction process at 900°C amounts to ~7% which corresponds well with eqn (1). For the alkoxide/carbonaceous gel, however, neither TG nor DTA analysis indicates the separation of the two reactions (1) and (2).

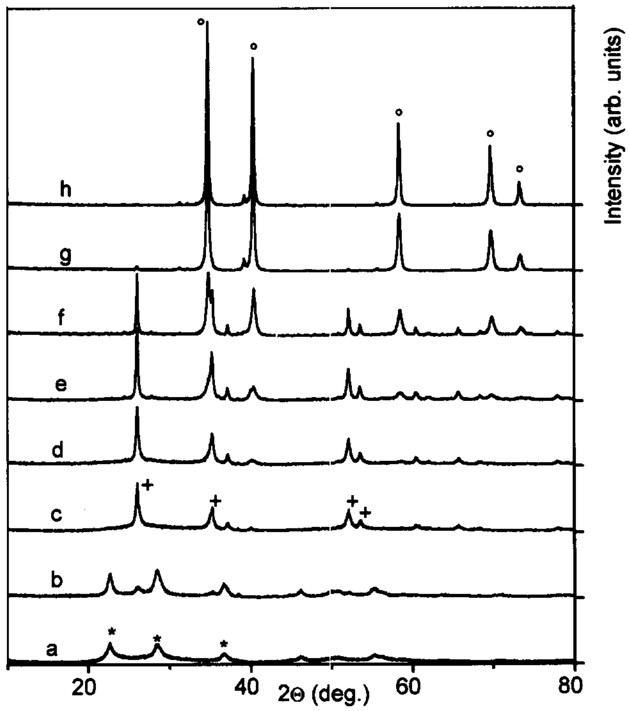
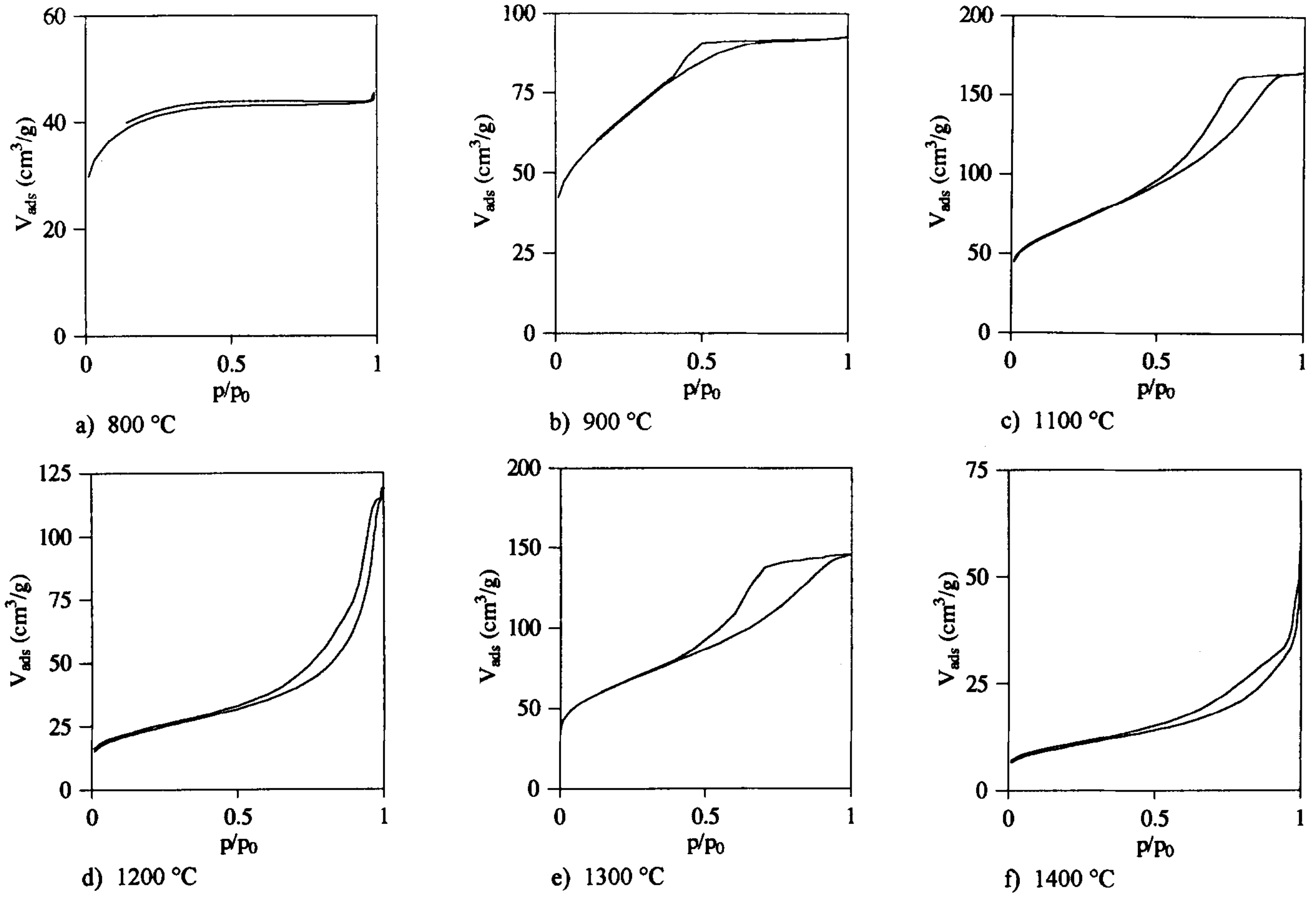


Fig. 4. X-ray diffraction patterns of niobium alkoxide/carbonaceous gel after heat treatment at temperatures from 700°C (a)–1400°C (h); (★: Nb_2O_5; +: NbO_2; O: NbC).

In the temperature range 1000–1200°C, the phases of tetragonal NbO_2 and cubic carbide (JCPDS card 38-1364) coexist. With temperature increase the intensities of the oxide lines decrease and those of the carbide lines increase. The 1300°C sample reveals only the carbide reflections. The presence of only NbC at this temperature is unexpected because the TG and DTA curves indicated the end of the carbothermal reduction for the gels at 1400°C. It can be inferred that the reduction reaction is time dependent. This suggests that the annealing time of 1 h and the lower heating rate in the oven experiment enable complete transformation into the carbide. The effect of the heating rate was confirmed by a TG/DTA run performed at a lower rate of 5 K/min. This led to a shift of the TG steps and DTA peaks by about 50°C to a lower temperature.

By using adsorption experiments, the thermal and X-ray analyses were supplemented. Measurement of the nitrogen adsorption shows that all xerogels remain poreless up to 600°C. Heating of the alkoxide/carbonaceous gel at 700°C and higher temperatures renders it porous, and the peroxide/saccharose gel becomes porous from 800°C. Some isotherms of the latter gel are depicted in Fig. 5; those of the alkoxide/carbonaceous gels have been reported and discussed previously.[15] The isotherms in Fig. 5 show the characteristics already found for the carbonaceous gels: with rising temperature their shape changes from Type I to Type IV. The isotherm Type I character and the non-closing of the desorption and adsorption branch of the 800°C sample are indicative of microporosity. At 900°C, a small hysteresis loop attributable to a Type H2 emerges in the p/p_0 range 0·4–0·8 (p = N_2 equilibrium pressure; p_0=N_2 saturation pressure), which is indicative of mesopores, appearing in addition to micropores. With further increase in temperature the hysteresis loop becomes broader, and it repeatedly alters between Type H2 and H3 (Fig. 5).

The BET specific surface areas calculated from the isotherms after heat treatment at different temperatures are shown in Fig. 6 for the niobium peroxide/saccharose as well as the niobium alkoxide/carbonaceous gel. The BET values reveal two maxima centred at about those temperatures where hysteresis Type H2 loops are observed, and where the TG/DTG curves show main mass loss steps for these gels. The pore volume distributions in the pore range 1–100 nm have been calculated from the adsorption branches of the isotherms. Some examples are presented in Fig. 7. The maxima of the pore radii at all temperatures are compiled in Table 1. As expected from the shapes of the isotherms, the pores of the gels annealed at temperatures lower than 900°C, i.e. before the carbothermal reduction starts, must have radii in the micropore range or at its upper limit. The micropore volume at the lowest temperatures exceeds the mesopore volume (Table 1). The mesopores formed at higher temperatures are mainly



a) 800 °C b) 900 °C c) 1100 °C

d) 1200 °C e) 1300 °C f) 1400 °C

Fig. 5. N_2 sorption isotherms of niobium peroxide/saccharose gel after heat treatment at various temperatures.

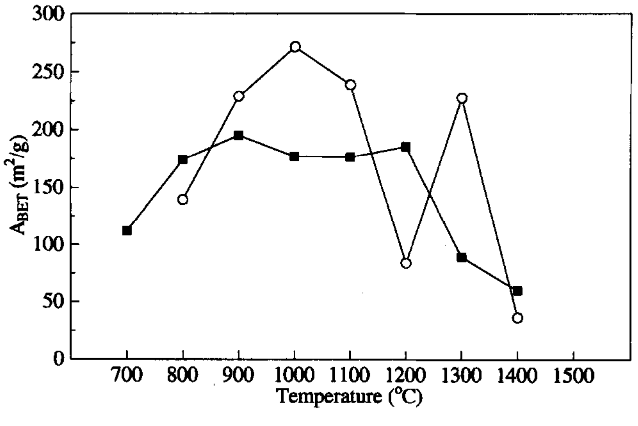


Fig. 6. BET surface areas of reaction products of niobium alkoxide/carbonaceous gel (■) and niobium peroxide/saccharose (●).

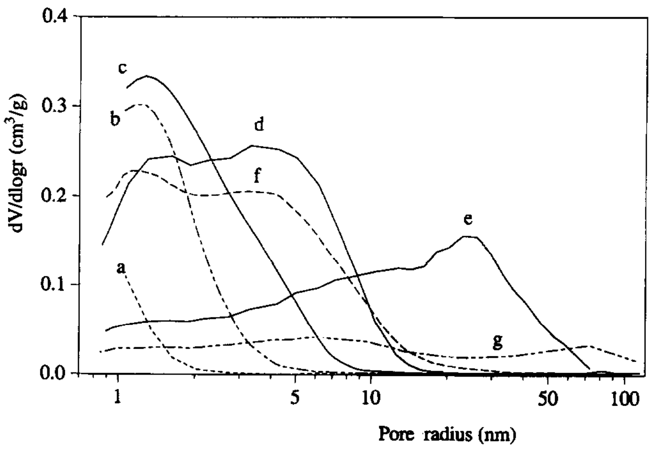


Fig. 7. Pore volume distributions of niobium peroxide/saccharose gel after heat treatment at temperatures from 800°C (a)–1400°C (g).

Table 1. Pore volume for range of pore radii 1–100 nm (V_{1-100}), micropore volume (V_{mi}) and pore radius maximum (R_{max}) of niobium and tantalum gel systems at different annealing temperatures (T)

	Nb peroxide/saccharose			*Nb alkoxide/carbonaceous gel*			*Ta peroxide/saccharose*			*Ta alkoxide/carbonaceous gel*		
T (°C)	V_{1-100} (cm³/g)	V_{mi} (cm³/g)	R_{max} (nm)	V_{1-100} (cm³/g)	V_{mi} (cm³/g)	R_{max} (nm)	V_{1-100} (cm³/g)	V_{mi} (cm³/g)	R_{max} (nm)	V_{1-100} (cm³/g)	V_{mi} (cm³/g)	R_{max} (nm)
700				0·021	0·023	<1				0·001	0	<1
800	0·023	0·033	<1	0·093	0·019	<1				0·013	0·015	<1
900	0·114	0·017	~1·2	0·139	0·015	~1·2	0·018	0·009	<1; 3	0·032	0·023	<1
1000	0·184	0·020	~1·2	0·152	0·017	1·2; 4	0·063	0·019	<1; 3	0·068	0·024	~1·2
1100	0·243	0·019	1·2; 4	0·191	0·018	1·2; 5	0·115	0·016	~1·2	0·102	0·021	2·8
1200	0·177	0·008	25	0·260	0·022	6·0	0·108	0·006	1·2; 3–4	0·126	0·025	3–4
1300	0·209	0·019	1·2; 5	0·262	0·007	16	0·113	0·009	2·8	0·191	0·006	5·0
1400	0·066	0	~70	0·215	0·004	20	0·025	0	2·8; 15	0·130	0·008	5·0
1500							0·21		2·8; 20	0·063		6·0

centred in two distribution ranges, one with radii of 3–5 nm, and the other, having radii above 10 nm, which extends for the final product at 1400°C up to the macropore range. The distribution maximum at the bigger radii is observed for all systems, including the tantalum systems (see later), and is connected with the occurrence of a Type H3 hysteresis loop.

3.2 The tantalum systems

Figures 8–10 show the TG and DTA curves for the mixture Ta_2O_5/carbon black, the pure peroxide gel, and the binary peroxide/saccharose and alkoxide/carbonaceous gel. No mass losses were found in the TG curve in Fig. 8 for the oxide/carbon black mixture up to about 1300°C. At higher temperatures, the carbothermal reduction gives rise to a TG step and an endothermic DTA peak, both centred at about 1450°C. X-ray analyses of annealed samples gave no hints on the formation of any tantalum suboxide. Thus, the reduction proceeds directly to TaC according to

$$Ta_2O_5 + 7\,C \rightarrow 2\,TaC + 5\,CO \tag{3}$$

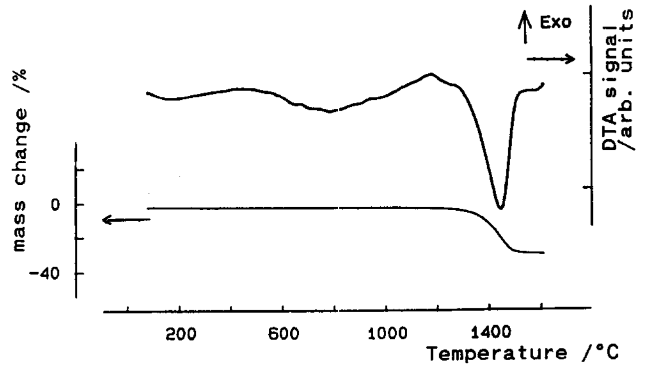


Fig. 8. TG/DTA diagram of Ta_2O_5/carbon black mixture.

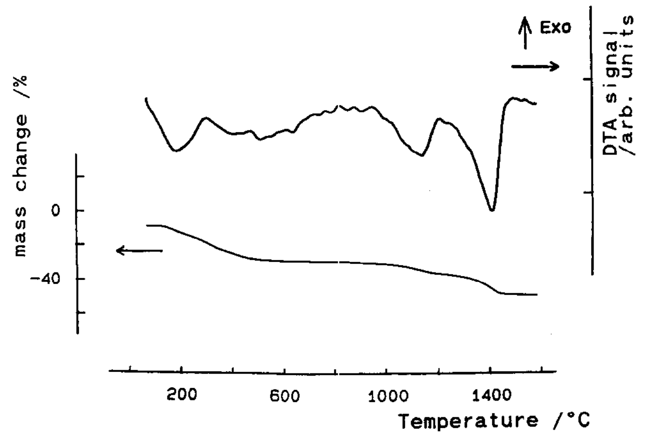


Fig. 9. TG/DTA diagram of tantalum alkoxide/carbonaceous gel.

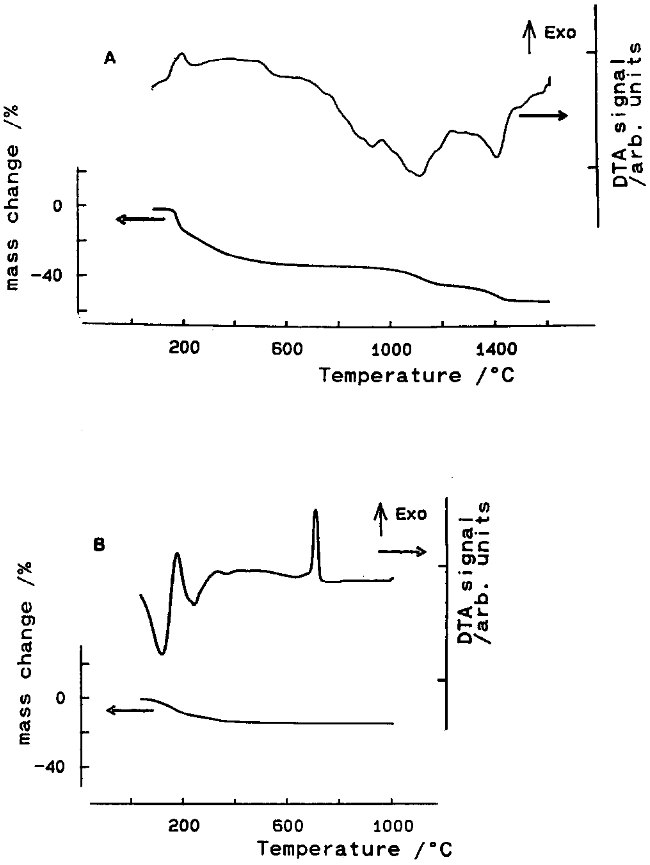


Fig. 10. TG/DTA diagrams of tantalum peroxide/saccharose gel (A) and tantalum peroxide gel (B).

The mass loss behaviour of alkoxide/carbonaceous gel up to 600°C, showing several overlapping steps (Fig. 9), resembles that of the corresponding niobium gel. The steps are attributable to the pyrolysis of the carbonaceous gel constituent and to the loss of water and organic groups bound to tantalum oxide. The subsequent region of a relatively constant mass is broader than for niobium and extends to about 950°C. Above this temperature, two reduction steps are perceptible in the TG as well as the DTA curve. In comparison with the niobium system, both steps are shifted by about 100°C to a higher temperature.

The binary peroxide/saccharose gel shows a strong TG mass loss step for the peroxide decomposition at about 190°C coupled with an exothermal DTA peak (Fig. 10(A)). The same thermal effect is found for the pure tantalum peroxide gel in Fig.10(B). In contrast to the binary gel, where no crystallization peak occurs, an intensive exothermic DTA peak at 720°C can be detected for the pure peroxide gel. This peak is due to the crystallization of Ta_2O_5 in the orthorhombic form as confirmed by X-ray diffraction. A gradual mass loss without DTA characteristics is found up to 600°C for the pyrolysis of saccharose. Between 600 and 1000°C, the mass loss of the peroxide/saccharose gel is limited to <2%. Beyond 1000°C, an increasing mass loss is associated with the release of CO, indicating the occurrence of the carbothermal reduction. The reduction proceeds in two steps at nearly the same temperature as for the alkoxide/carbonaceous gel (Fig. 9), showing that these reactions are almost identical.

X-ray diffraction shows that the alkoxide/carbonaceous gel is completely amorphous up to 700°C, and the peroxide/saccharose up to 800°C. At 800 and 900°C, respectively, both products reveal some XRD bands at positions where orthorhombic Ta_2O_5 has the strongest diffraction peaks. These bands are notably broadened showing that amorphous Ta_2O_5 has transformed in the orthorhombic phase with crystallite sizes in the nanometer range. Calcination at higher temperature leads to a narrowing of these XRD lines due to crystal growth; above 900°C the patterns of both gels are almost equal. The XRD patterns of the alkoxide/carbonaceous gel are shown in Fig. 11. At 1000°C, in addition to the Ta_2O_5 lines both gels show some weak lines attributable to the cubic tantalum carbide (JCPDS card 35-801). A further temperature increase renders the carbide lines narrower and stronger and those of Ta_2O_5 weaker. Crystallite sizes of the carbide and oxide as estimated using line broadening analysis are listed in Table 2. The only crystalline phase present at 1400°C is TaC (the temperature discrepancy with the TG/DTA data is due to the time-dependence of the reduction reactions).

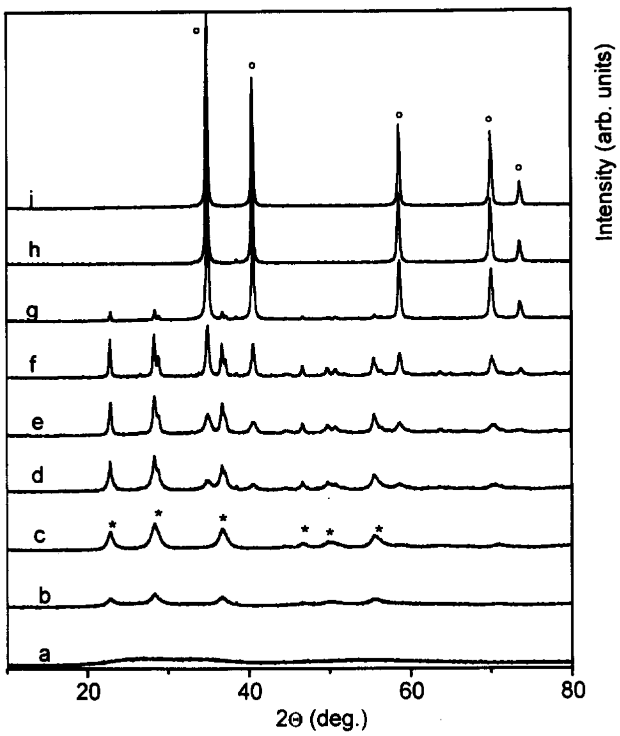


Fig. 11. X-ray diffraction patterns of tantalum alkoxide/carbonaceous gel after heat treatment from 700°C (a)–1500°C (i); (★: Ta_2O_5; O; TaC).

Nitrogen adsorption studies supported the X-ray and TG/DTA data well. The amorphous xerogels were found to be non-porous. Parallel to the crystallization of Ta_2O_5 at 800 and 900°C, respectively, porosity begins to appear for both binary gels. The isotherms of the heated alkoxide/carbonaceous gel reported elsewhere,[15] and those of the peroxide/saccharose gel resemble those of the corresponding niobium gels with the exception that the characteristic features are shifted by about 100°C to higher temperatures. Again, the shapes of the isotherms change with rising temperature from Type I to Type IV and those of the hysteresis

Table 2· Crystallite sizes (d) of Nb_2O_5, NbO_2, Ta_2O_5, NbC and TaC in binary alkoxide/carbonaceous gels at different annealing temperatures (T)

	Niobium gel		*Tantalum gel*	
T (°C)	d_{oxide} (nm)	$d_{carbide}$ (nm)	d_{oxide} (nm)	$d_{carbide}$ (nm)
700	5–8[a]			
800	11[a]		8	
900	18–21[b]		11	
1000	21–24[b]		17	11
1100	36[b]	12	33	12
1200	96[b]	21	53	27
1300	250[b]	29	111	41
1400		47		50
1500				66

[a]Nb_2O_5; [b]NbO_2.

loops in the sequence H4 to H2 and finally to a loop which may be described as a mixed type between H1 and H3. For tantalum peroxide/saccharose the final hysteresis loop (at 1500°C) more closely resembles Type H3, and for the tantalum alkoxide/carbonaceous gel it more closely resembles the Type H1. The maxima of the pore radii of the distribution curves listed in Table 1 in general show an increase in the radii with rising temperature. The BET surface areas in Fig. 12 reveal two maximum values for intermediate products reflecting that the carbothermal reduction proceeds in two main steps as found by TG/DTA; micropore volumes also reveal maxima in these temperature ranges (Table 1). With the approach to the final temperature of 1500°C the surface areas decrease.

Values of the chemical analyses of tantalum carbide obtained at 1500°C are listed in Table 3 together with those of NbC obtained at 1400°C. Obviously, the final products contain 1–2% of non-bonded carbon (theoretical value for NbC: 11·43%; and for TaC: 6·22%) and about 1% of oxygen. A certain content of N in the peroxide gels may be associated with NH_3 caught by the hydroxides during their precipitation. Table 3 also comprises the lattice parameters (*a*) of TaC after 1500°C and NbC after 1400°C. These parameters are very close to those reported in the JCPDS cards 35-801 for TaC: $a = 4{\cdot}4547(2)$Å and 38-1364 for NbC: $a = 4{\cdot}4698(2)$Å.

Examination by scanning electron microscopy revealed different morphologies for the systems studied. Figure 13 shows micrographs of surfaces of a typical intermediate and some final reaction products. The surface of pyrolysed gels (600°C) is flat and does not reveal any structural characteristics (not shown in Fig. 13). After the onset of the reduction processes, however, isolated grains appear. The micrograph in Fig. 13(A) is a typical example for this intermediate reaction stage, showing a high dispersity of the grains which comprise TaC as well as Ta_2O_5 particles. Heat treatment of the tantalum gels at the final temperatures, however, forms TaC grains of an inhomogeneous size distribution. Figure 13(B) shows that well-crystallized TaC grains of about 1 μm in size are present simultaneously with aggregates formed from much smaller size (at about 100 nm). Contrary to the tantalum gel, the gel-derived NbC reveals a widely homogeneous grain distribution at 1400°C (Fig. 13(C)). The morphology of the carbides obtained from the M_2O_5/carbon black mixtures is very different to that of the gel systems. Only large particles were observed for TaC powders synthesized at 1500°C from that mixture (Fig. 13(D)).

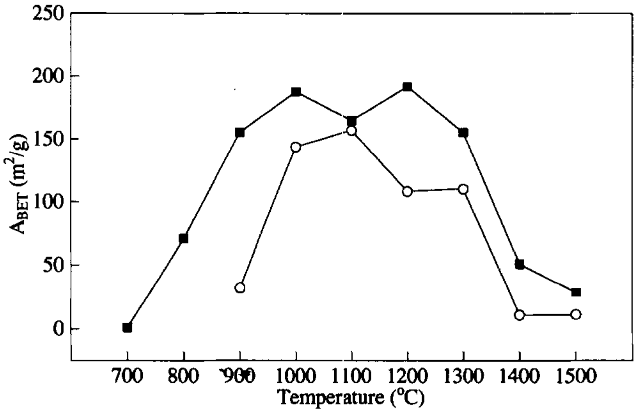


Fig. 12. BET surface areas of reaction products of tantalum alkoxide/carbonaceous gel (■) and tantalum peroxide/saccharose gel (○).

Table 3. Chemical analyses of non-metals and lattice parameters (*a*) of carbides prepared from the niobium peroxide/saccharose gel at 1400°C and from tantalum peroxide/saccharose gel at 1500°C

	C_{total} *(wt%)*	*Oxygen (wt%)*	*Nitrogen (wt%)*	a *(Å)*
NbC	12·71	1·16	0·32	4·4708 (2)
TaC	8·02	1·07	0·23	4·4560 (2)

4 Discussion

The facility of transition metals to form oxide sols either from alkoxides or peroxo acids has proved an important factor in their success in the sol–gel synthesis of preceramic materials. Chemical additives as organic acids, polyols and diketones are always known for the stabilization of sols. Here, hydrogen peroxide is additionally used for the preparation of binary organic–inorganic sols. Successive processing, mostly heating, then transforms the mixed sols into diphasic gels by condensation and polymerization of the transition metal component. The oxide particles and the organic materials are mixed very intimately, at least on a colloidal scale. Functional groups present in the organic materials may be bound to the surface sites of the colloidal oxide particles. Heat treatment up to about 600°C converts the organic gel constituents into almost pure carbon and the peroxide and oxide hydrates into the oxides. The precursors thus formed are of high reactivity, showing lower reduction temperatures (by 250–300°C) than physical mixtures of oxides and carbon black.

For comparative studies the thermodynamic feasibility of the carbothermal reduction reactions (1), (2) and (3) was calculated using the data of Ref.16. The calculated free enthalpies in Fig. 14

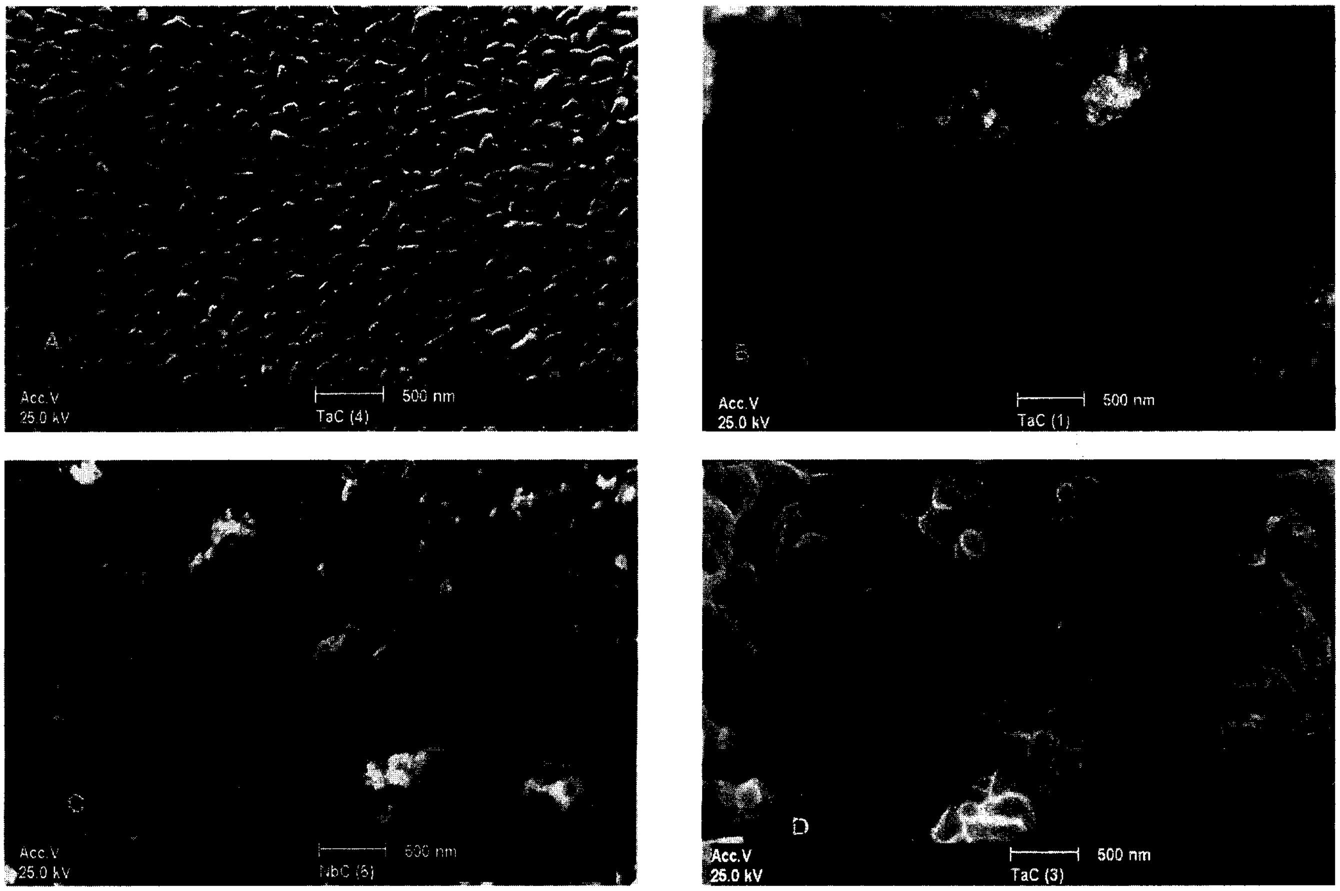


Fig. 13. Scanning electron micrographs of Ta alkoxide/carbonaceous gel at 1200°C (A); Ta alkoxide/carbonaceous gel at 1500°C (B); Nb alkoxide/carbonaceous gel at 1400°C (C); and Ta_2O_5/carbon black at 1500°C (D).

become negative for the NbO_2 and NbC formation at nearly the same temperature (about 950°C) and for the formation of TaC at 1100°C. Although comparison of these thermodynamic data with the present experimental results is not strictly valid because the former relate to equilibrium conditions and graphite as carbon reactant, some interesting points emerge. The first major point is that experimentally the NbO_2 formation is separated from the NbC formation by a notable shift to lower temperatures. The DTA and TG curves in Figs 1–3 reveal separate peaks for Nb_2O_5/carbon black and the peroxide/saccharose gel, and a tailing of the first reduction peak at the low-temperature side for the alkoxide/carbonaceous gel. A second observation is that the onset of the carbide formation for all gel systems nearly agrees with the temperatures predicted from the thermodynamic calculations. The formation of NbC and TaC at these low temperatures is not unexpected; it has also been found for polymeric systems[4,7] and for solid-state reactions[17] with carbon contents exceeding the molar ratio $C/M_2O_5 = 7$.

The lower reduction onset in the gels is thought to be attributable to the dispersion and structure of carbon in the precursor materials. Owing to the gel procedure an intimate mixture of the oxides and carbon compounds is achieved. Absence of melting and crystallization processes during the gel degradation are two important factors to ensure that the homogeneous distribution is widely conserved during pyrolysis. As compared to conventional oxide/carbon mixtures, the diffusion distances are considerably shortened, and consequently the reaction kinetics is much improved. Further reaction progress, however, may then be limited by time-consuming diffusion processes. The smaller the size of the oxide particles the smaller the limiting effect. The presence of oxide particles in the nanometer range in the precursors ensures short diffusion distances. Consequently, the capacity of the carbon network to restrain nucleation and crystallite growth of the dispersed oxides (Tables 2 and 4) is another factor (the *constraint effect*) for the lowering of the reduction temperature.

The crystallization temperatures of Nb_2O_5 and Ta_2O_5 in the binary gels are listed in Table 4 together with those observed for the pure peroxide gels and those reported elsewhere for oxide gels derived from alkoxide hydrolysis.[18,19] Compared to the single oxide gels, an increase in the crystallization temperatures by 100–200°C is stated for all binary systems. This increase may be explained by the fact that the oxides are constrained in the carbon matrix. An increase in crystallization tem-

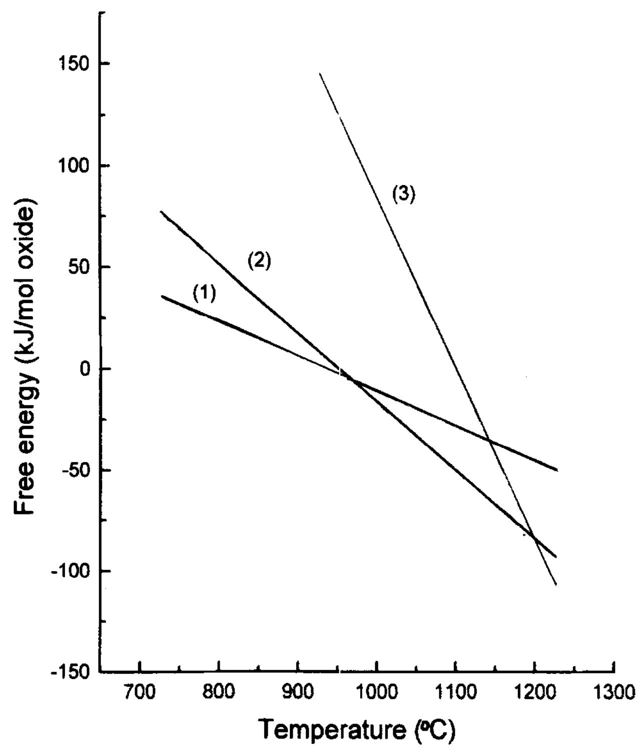


Fig. 14. Free enthalpies of the reduction reactions (1), (2) and (3).

peratures has been found recently for SiO_2/carbonaceous and ZrO_2/carbonaceous gels[10,11] also. Line broadening analysis shows that Nb_2O_5 and Ta_2O_5 begin to crystallize with sizes in the nanometer range (Table 2). The crystallite sizes of Nb_2O_5 and Ta_2O_5 are ~8 nm at 700 and 800°C, respectively; they grow to 11 nm up to the temperature where the reduction starts.

A *structural effect* is concerned with the kind of carbon produced during the gel pyrolysis at 600–800°C. It is well known that a pyrolysis coke at these temperatures has a structure far from that of graphite. In a variety of publications it was found that the reactivity of the carbon reactants in carbothermal reduction is higher the further their structure is from that of graphite.[17,20,21] Thus, in our systems we are dealing with a highly reactive carbon.

Phase transformation may be another promoting factor for the carbothermal reduction. Transformation of orthorhombic to monoclinic Nb_2O_5 is known to occur at ~900°C, the temperature at which the reduction in the gels begins. Generally, a phase transformation at the start of a solid-state reaction should lead to a higher reactivity (*Hedvall effect*). Considering that Nb_2O_5 is orthorhombic in the pyrolysed gels and monoclinic in the oxide/carbon black mixture, some acceleration to form NbO_2 seems likely in the former. For the higher temperature steps, however, this acceleration may no longer be valid.

Table 4. Crystallization temperatures (°C) of Nb_2O_5 and Ta_2O_5 in different gel systems

	Nb system	*Ta system*
Single alkoxide gel	492[a]	550[b]
Binary alkoxide/carbonaceous gel	640	700–800
Single peroxide gel	540	720
Binary peroxide/saccharose gel	700–800	800–900

[a]Ref. 16; [b]Ref. 17.

The carbide formation in the gels proceeds in a broad temperature range showing two TG and DTA extrema in each case. These findings are surprising because the M_2O_5/carbon black mixtures did not indicate a two step mechanism for these reactions. No additional XRD lines of suboxides, except NbO_2, but only lines of an f.c.c. phase attributable to carbides or oxycarbides, have been found. The formation of oxycarbides preceding the carbide formation is well known for the transition metals of the fourth group. Oxycarbides of niobium and tantalum, however, have been reported only as metastable forms with low oxygen contents;[22,23] the maximum oxygen content in the cubic tantalum carbide is lower than 0·02 at%.[24] These oxycarbides exist merely under a high CO partial pressure (e.g. in large bulks), and they readily decompose into the respective carbides and oxides. Under the preparation conditions used here with flowing argon, their formation is very unlikely. Moreover, the supposed decomposition products are evidenced side by side from 1100°C up to the final DTA peaks. Thus, it is to be assumed that oxycarbides, if formed at all, will occur at the start of carburization and decompose with temperature increase.

The rates of formation of NbC and TaC are low at the start of the carburization. They increase only slowly with rising temperature as inferred from the intensity change of the carbide and oxide XRD lines in Figs 4 and 11. These findings may be due to competition between carbide formation and crystallite growth of the oxides into less reactive particles, as concluded from the crystallite size data of the carbides and oxides (Table 2).

Adsorption measurements have shown the porous structure of heat-treated gels. Moreover, nitrogen adsorption has proved useful in following the thermal reaction sequences. During heating, specific surface area and pore distribution change in a characteristic way, reflecting that the carbothermal reduction proceeds at least in two steps. The first increase in porosity generating a high portion of micropores is probably caused by the crystallization of Nb_2O_5 or Ta_2O_5 at 700–900°C. Presumably, structural reorganization in the gels is connected with an increase in density and produces cracks and voids with micropore diameters. During the first reduction step mesopores with radii from 2·8 to 5 nm are additionally formed by expulsion of CO; however, the conversion of the oxides into carbides is incomplete. In the succeeding temperature range at 1100–1200°C, crystal growth of the oxides and carbides (Table 2) are the main processes, leading to a decrease in the BET values and pore volumes, and to pore widening (Table 1). During the second reduction step BET values and pore volumes pass a second maximum, and additional mesopores (mostly at 2·8–5 nm) are generated by chemical reactions. Crystal growth and small neck-sintering during final heating change the pore systems, and intercrystalline pores with radii >15 nm are formed. The approach of the isotherms to Type IV and of the hysteresis loops to Type H3 is indicative of agglomerate structures, and SEM micrographs support this assumption.

Examination by SEM reveals that carbides have been obtained from gel systems with a grain size of 1 μm or less. It is supposed that such small grain sizes (see Fig. 13(A)) are the consequence of homogeneous nucleation and crystal growth in the gels. In the early reduction stage carbon may coat the oxide and carbide particles within the gel network and prevent their growth and aggregation. Consumption of carbon in the further reduction stages promotes growth processes of various kinds. The grain size distribution of the resulting TaC is less homogeneous than that of NbC. The reasons for this different behaviour are not clear at the present time. In order to prove more accurately the homogeneity of the carbides, thermogravimetric analyses were performed in an air flow. Recently it has been found that oxidation experiments can be used to determine particle size distributions of metal carbides.[25] Here, gels as well as physical mixtures were first heated under argon up to 1600°C, and after cooling they were reheated in air. Figure 15 depicts TG and DTA curves of the reheating experiments for the niobium alkoxide/carbonaceous gel and Nb_2O_5/carbon black, and Fig. 16 depicts those for tantalum peroxide/saccharose gel and Ta_2O_5/carbon black. These studies show that oxidation for the tantalum systems begins at a temperature about 100°C higher than that for the corresponding niobium systems. A major observation is that the oxidation of niobium samples covers a narrower temperature range than that of the tantalum samples. In terms of a particle size effect it is inferred that the size distribution of the NbC particles must be more homogeneous. Figure 16 shows that the oxidation of the tantalum saccharose sample (1600°C) proceeds in two steps, the highest being centred at about the temperature at which Ta_2O_5/carbon black oxidizes. These findings are consistent with the inhomogeneous grain size distribution in Fig. 13(B) and (D). Some humps or bends in the oxidation curves at 550–700°C may be due to the burn-off of residual carbon.

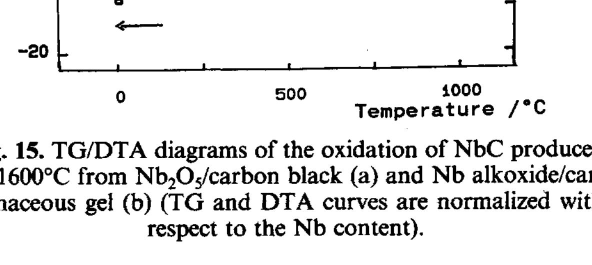


Fig. 15. TG/DTA diagrams of the oxidation of NbC produced at 1600°C from Nb_2O_5/carbon black (a) and Nb alkoxide/carbonaceous gel (b) (TG and DTA curves are normalized with respect to the Nb content).

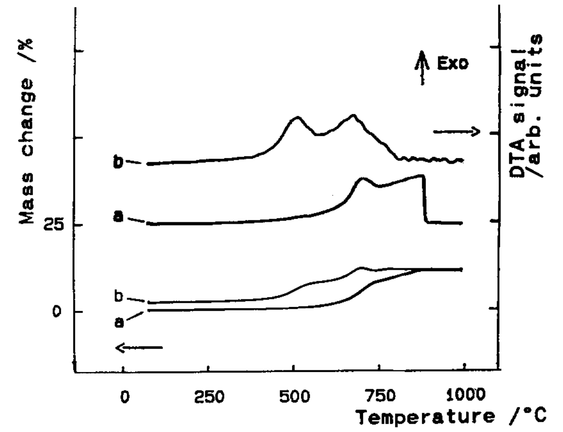


Fig. 16. TG/DTA diagrams of the oxidation of TaC produced at 1600°C from Ta_2O_5/carbon black (a) and Ta peroxide/saccharose gel (b) (TG and DTA curves are normalized with respect to the Ta content).

5 Conclusions

Binary organic–inorganic gels have been found to be advantageous precursors for the carbothermal formation of NbC and TaC. The gels can be prepared starting from (a) sols of the transition metal alkoxides or peroxo acids and (b) carbonaceous gel or saccharose. Pyrolysis transforms the gels into precursors which consist of nanometer sized M_2O_5 oxides dispersed in a carbon matrix and reveal a promoted reaction kinetics.

In comparison with physical mixtures of oxides with carbon black, the onset of the carbothermal reduction in the gels is lowered to modest temperatures, but no complete carbide formation is achieved at these temperatures. The role taken by the *in situ*-produced carbon in promoting the kinetics is that (1) it is intimately mixed with the oxides, (2) it hinders the nucleation and crystallite growth of the oxides and (3) it is of high reactivity. The thermal reaction sequences were investigated with X-ray, TG/DTA and adsorption experiments. It has been proved that nitrogen adsorption is a useful method for following these sequences. Throughout the thermal treatment the poreless gels change into microporous gels, then into mesoporous intermediary products, and finally into carbides with grain sizes of 1 μm and less and with an intercrystalline porosity. Hence, the sol–gel technique appears suitable for the production of preceramic materials and of submicrometer transition metal carbides which may be used in catalysis and ceramics.

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