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Studies on the Carbothermal Preparation of Titanium Carbide from Different Gel Precursors

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Abstract

Different mixed organic–inorganic gels as precursors for the synthesis of titanium carbide and oxycarbides have been prepared in aqueous and organic solutions starting either from rutile or titanium alkoxide. The sol–gel processes have been controlled by complexing additives such as H_2O_2, acetic acid or ethyl acetoacetate. Upon pyrolysis up to ~600°C, composites of finely divided particles of amorphous titania and carbon are formed. Monitoring of the high-temperature treatment by TG, XRD and nitrogen adsorption up to 1600°C revealed a three-step carbothermal reduction mechanism through lower titanium oxides and oxycarbides. The intimate mixture of titania and carbon leads to a considerable lowering of the onset of the reaction temperature in comparison with rutile/carbon black and rutile/gel mixtures. Delayed reactions in the final steps, however, may be due to the interruption of the intimate contact of the reactants by pore generation. During the high temperature processes microporous and mesoporous intermediate materials have been prepared; the final products at 1600°C are finely divided particles of oxycarbides with oxygen contents of 1·2–3·4 wt% and grain sizes lower than 1 µm. © 1998 Elsevier Science Limited. All rights reserved

Keywords: sol–gel processes, calcination, porosity, carbides, carbothermal reaction.

1 Introduction

In recent years, titanium carbide has received much attention as material for catalytical and electrochemical applications apart from its use in sintered composite materials, such as Al_2O_3–TiC composites. Carbothermal reduction of TiO_2 by solid carbon materials in inert atmosphere or in vacuum is the most effective method to produce titanium carbide for application in composite materials. With this method TiC with a predominant grain size greater than 1 μm and a low specific surface area can be obtained. The usage in catalytical and several advanced applications, however, requires materials of a low particle size and high specific surface area.

New synthesis routes to such TiC materials are based up to now on either gas–solid reactions[1] or gas phase reactions.[2] The carbothermal reduction of gel-derived and polymeric precursors should be advantageous, too. In attempting to retain in the product material the high surface area of starting materials (e.g. of carbon black), the carbon component was dispersed in a titania gel, and ultrafine titanium carbide could be prepared from this ‘seeded’ gel precursor.[3] The titania gel was obtained by hydrolysis of titanium alkoxide. The intimate mixing of reactants and the formation of amorphous titania instead using crystalline TiO_2 as the starting compound are essential advantages of gel routes.

A high degree of mixing is also made possible by using starting precursors in the form of polymers. The precursors of this second category, which are mostly prepared from titanium alkoxides by transesterification, contain Ti–O–C bonds. The carbon needed for carbothermal reduction is introduced either by the transesterification or by an additional reactant, e.g. phenolic resin or furfuryl alcohol.[4–6] Since polymer routes mostly proceed through a gel stage they are called sometimes also as gel routes. Recently, a polymer synthesis for a TiC precursor which includes transesterification as well as hydrolysis has been reported.[7]

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This paper deals with gel types differing from those mentioned above. Carbonaceous hydrogels, recently synthesized from pitches,[8–10] offer the possibility of the formation of binary gels in which one constituent is an organic network. These carbonaceous hydrogels have proved as useful starting components for the carbothermal synthesis of fine zirconium, niobium and tantalum carbides from gel-derived precursors.[11,12] For the preparation of TiC, two mixed types with the carbonaceous gel are prepared in this work; the first one includes dispersion of rutile in the carbonaceous gel in order to produce a seeded gel, and the second one is a binary gel in which both the organic and the inorganic component are gel formers. Obviously, the homogeneity of the reactants in the binary gel should be higher than in the 'seeded' gel.

In order to study the influence of different carbon sources on the carbothermal reduction process, the organic gel constituent is substituted by saccharose in a third gel type. It is expected that the coke produced by pyrolysis of saccharose is more reactive than the coke obtained from carbonaceous gel.

The degree of densification in the gel precursors seems to be another important factor that influences the reaction rate between the inorganic and carbon compound. A characteristic feature of hydrogels is the presence of large pores which are filled with water, based on the interaction between OH-groups of the pore walls and the water molecules. The larger the pores are the more inhomogeneous the gel precursor can be considered. In order to increase the densification in the precursors, two polymeric organogels have been prepared either with acetic acid or ethylene glycol but without the addition of any water. The subject of the present paper is the preparation of different gel precursors and the study of the effects of homogeneity, densification and reactivity of the reactants on the carbothermal reduction processes. The carbothermal reduction reactions in the gels are followed by simultaneous thermogravimetric and differential thermal analysis (TG/DTA), X-ray diffraction (XRD), nitrogen adsorption and scanning electron microscopy (SEM).

2 Experimental

2.1 Gel synthesis

2.1.1 Rutile/carbonaceous hydrogel

First 6·7 g of the dried carbonaceous gel were suspended in a mixture of 70 ml distilled water and 5 ml 30% hydrogenperoxide and then heated at 80°C up to a carbonaceous hydrosol has formed. Next, 8 g rutile of a grain size of 0·4–1·0 μm were dispersed in the hydrosol under stirring at 80°C. By cooling down to room temperature the mixture transformed into a gel stage (the solutions of carbonaceous gels change between gel and sol upon heating and cooling).[9,10] The rutile/gel mixture was dried at room temperature and later at 110°C to obtain the precursor for the thermal treatment.

2.1.2 Titanium alkoxide/carbonaceous hydrogel

First, 6·81 g titanium(IV)n-butoxide (0·02 mol) (Fluka AG) dissolved in 6 ml n-butanol were added drop by drop under stirring to a solution of 4 ml 30% aqueous hydrogenperoxide in 25 ml ethanol at 0°C. Immediately after that mixing, a solution of 1·00 g of the dried carbonaceous gel in a mixture of 5 ml distilled water, 1 ml 30% hydrogen peroxide and 15 ml ethanol were added under successive stirring at 0°C (the precursors A-D in Table 1 were prepared with different quantities of the carbonaceous gel: A, 0·75 g; B, 1·00g; C 1·25g; D 1·50 g). The carbonaceous gel was prepared according to Ref.9 and 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. Finally, 1 g glycerol was added in each case to the mixed solutions. Gel formation took place at room temperature while most of the H_2O_2 decomposed. The solvents were evaporated firstly at room temperature and afterwards at 110°C.

2.1.3 Titanium peroxide/saccharose hydrogel

First, 5·68 g titanium(IV) isopropoxide (0·02 mol) (Fluka AG) were mixed with 40 ml 20% aqueous hydrogenperoxide at 0°C and stirred for 0·5 h at 0°C until a translucent, red-orange sol had formed. The orange sol was acidic, showing that titanium peroxoacids have formed in the solution. Then 2·90 g saccharose dissolved in 10 ml distilled water were added, and the mixed solution was stirred at room temperature. Whilst most of excess H_2O_2 decomposed, the sol converted into a yellow gel. Drying first at 60°C and later at 110°C led to a xerogel.

2.1.4 Titanium acetate/saccharose organogel

First, 2·26 g saccharose were dissolved in 10 ml acetic acid under heating at 80°C. Then 6·81 titanium(IV) n-butoxide (0·02 mol) (Fluka AG) were weighed to the solution at room temperature;

Table 1. Total carbon content (C), BET surface areas, and crystallite sizes (*d*) of the reaction products of different titanium alkoxide/carbonaceous gels after annealing at 1500°C

Gel type	*C* (*wt*%)	*BET* ($m^2 g^{-1}$)	d (*nm*)
A	15·7	10	54
B	21·1	86	44
C	27·1	181	39
D	32·7	298	37

successive stirring led to a deep red solution (sol). Gelling began at room temperature perceptible by the increase of the viscosity, and after 1–2 h a stiff gel had formed. After evaporation of residual acetic acid and generated butyl acetate the gel precursor was obtained.

2.1.5 Titanium glycolate/ethyl acetoacetate organogel

First, 6·81 g titanium(IV) n-butoxide (Fluka AG) were added to a mixture of 10 ml ethyl acetoacetate and 5 ml n-butanol under stirring. Then the solution was heated at 80°C under stirring for 30 min. After cooling the solution to room temperature 1·25 g ethylene glycol were added under stirring. Succeeding heating at 120°C transformed the red solution (sol) into a gel. The gel precursor was obtained after drying at 150°C.

For comparing with the gel precursors a mixture of rutile (d = 0·4–1·0 μm) and acetylene black was prepared by homogenizing in a vibration mill for 5 h.

2.2 Heat treatment

The xerogels were annealed in graphite boats using an alumina tube furnace (Carbolite Furnace Limited) at 200–1600°C with 50 or 100°C intervals in flowing argon. The heating rate was 10°C min, and the holding time at the reaction temperature was 1 h.

2.3 Characterization

Thermal behaviour of the xerogels and the rutile/carbon black mixture in argon was studied by simultaneous TG/DTA using a SETARAM TAG 24 thermoanalyzer. Subsequent TG/DTA in air of the final heating products allowed to determine their titanium content. The heating rate was 15°C min^{-1} in all cases. Chemical analyses of the non-metals were performed using the CHN-analyser EA 1110 (CE Instruments). Oxygen and nitrogen were additionally determined with LECO TC-436, total carbon with LECO CS-444, and free carbon by dissolving all components except free carbon in a HF/HNO$_3$ mixture followed by filtration, combustion and conductometric determination of CO$_2$.

Standard X-ray diffractometry with nickel-filtered Cu K$_\alpha$ radiation was used to determine the crystalline phases present in the heat treated samples. SEM studies were performed using a Stereoscan 260 (Leica) and a high-resolution SEM (Leo). Measurements of nitrogen adsorption/desorption at 77 K were performed after drying and degassing the samples under vacuum at 300°C using an ASAP 2010 instrument of Micromeritics. BET surface areas and *t*-plots (micropore surface areas and volumina) according to Harkins and Jura were calculated from the nitrogen isotherms.

3 Results and Discussion

3.1 Chemistry of gel formation

During the reaction of titanium alkoxides with water spontaneous precipitation occurs in consequence of successive hydrolysis and condensation reactions forming oxo bridges. The reaction with ethylene glycol or saccharose leads to precipitates by trans-esterification and condensation. In the case of ethylene glycol, glycolate bridges of the type –Ti–O–CH$_2$–CH$_2$–O–Ti– are formed. However, when water or ethylene glycol react with transition metal alkoxides in the presence of such organic additives as organic acids or β-diketones, stable sols can be formed.[13,14]

Complexation by these bidentate chelating ligands saturates the maximum coordination number of the transition metals and controls the successive condensations. Here acetic acid, ethyl acetoacetate, and additionally hydrogenperoxide are used for the production of stable alkoxide-derived sols in aqueous as well as non-aqueous solvents.

In organic solvents the bonds of titanium to chelating ligands are more stable against hydrolysis and condensation reactions than those to alkoxy groups.[14] Moreover, acetic acid is often used for controlled sol–gel processes without addition of water.[15,16] The water necessary for hydrolysis is generated *in situ* by esterification of acetic acid with alcohol released by the preceding formation of acetate derivatives of the alkoxides. In this paper it is shown that this method is applicable also for the preparation of a multicomponent gel, a titanium acetate/ saccharose organogel.

Recently, H$_2$O$_2$ has proved as a useful reagent for sol–gel processes of transition metals of the Va and VIa group[12,17] in aqeous media. We have found that titanium alkoxides are soluble both in aqueous and alcoholic hydrogenperoxide solutions; the peroxoacids formed at first condense into peroxide. Presumably, the O$_2$ peroxo group behaves in solution as a bidentate complexing ligand and can satisfy the coordination number. The existence of bidentate O$_2$ ligands has been concluded from IR spectral investigations for titanium peroxides and peroxometallates.[18,19] The titanium peroxide sol, however, is less stable than its analogous types of the Va and VIa group elements. It readily transforms into a gel upon partial decomposition of O$_2$ groups at room temperature (complete decomposition of the O$_2$ groups is reported at 88°C).[18] The length of time of the stability of the sol is sufficient for the preparation of a mixed inorganic/organic sol.

The mixed sol is prepared by adding the organic compound (carbonaceous gel, saccharose) to the freshly prepared peroxide sol; no precipitation is observed in this stage of processing. Conversion into mixed gels occurs at room temperature after partial decomposition of excess H_2O_2 and the complexing O_2 groups. It is thought that the gel former at the beginning is a titanium oxide/peroxide hydrate, and the organic compounds are fixed via functional groups (OH, COOH, SO_3H) to the gel network.

3.2 Thermal decomposition of the gel precursors

Calcination of the titania constituent and conversion of the organic gel compounds into almost pure carbon proceed during the first pyrolysis stage up to 500–600°C. Simultaneous TG/DTA analyses give a more detailed picture of the pyrolysis reactions. Figure 1 shows the TG and DTA curves for the rutile/carbonaceous and alkoxide/carbonaceous gel together with those of a rutile/carbon black mixture for reasons of comparison. Clearly, the mass of the rutile/carbon mixture is constant up to the reduction start at ~1150°C. The TG curves of the mixed gels can be roughly divided in three sections: (1) the decomposition of the gel constituents, followed by (2) a section of nearly constant mass (~600–900°C), and (3) the carbothermal reduction reactions at high temperatures (> 900°C).

The thermal behaviour of rutile/carbonaceous gel resembles that of the pure carbonaceous gel reported recently.[10] The TG curve reveals two decomposition mass loss steps at ~140 and 250°C which may be attributed to the loss of entrapped water, and the decomposition of the functional groups (OH, COOH, SO_3H) of the carbonaceous gel. Both steps coincide with endothermic DTA peaks. For the alkoxide/carbonaceous gel the decomposition is extended to higher temperatures, showing an additional DTA minimum at ~400°C. Presumably, this decomposition step stems from functional groups fixed to the titania network. The TG curves of the other binary gels show that the decomposition reactions proceed in several overlapping steps, too (Fig. 2).

All gel precursors with the exception of rutile/carbonaceous gel were identified as being X-ray amorphous up to 500–600°C. TiO_2 begins to crystallize in the anatase form at ~600°C in the alkoxide/carboneceous gel and at 700°C in the saccharose containing gels (no thermal effects have been observed for the crystallization of anatase in the DTA curves). Such high temperatures for the crystallization of TiO_2 gel materials are surprising because it has been found that gel-derived TiO_2 powder became crystalline already at 200°C[20] or even at room temperature after a long time.[21] The inhibition of the crystallization in the mixed gels up to temperatures of 600°C may be explained by two effects: the steric hindrance by organic groups, and the fact that amorphous TiO_2 is constrained in a carbon matrix. Hindrance of crystallization by functional groups which are bound with TiO_2 and prevent the reconstruction of the amorphous Ti–O network has been found in hydrolyzed titanium alkoxides.[21] When all organic material is converted into almost pure carbon, amorphous TiO_2 can be thought to be constrained in a rigid carbon matrix which acts as a hindrance for the crystallization. A delayed crystallization has also been found for ZrO_2, Nb_2O_5 and Ta_2O_5 when these oxides are constrained in a carbon matrix.[11,12]

The diffraction lines of the anatase phase at the beginning of crystallization are very broad, showing that anatase is formed as crystallites of nanometer sizes. The crystallites grow only insignificantly upon heating up to 800°C (6·5 nm); the pattern of

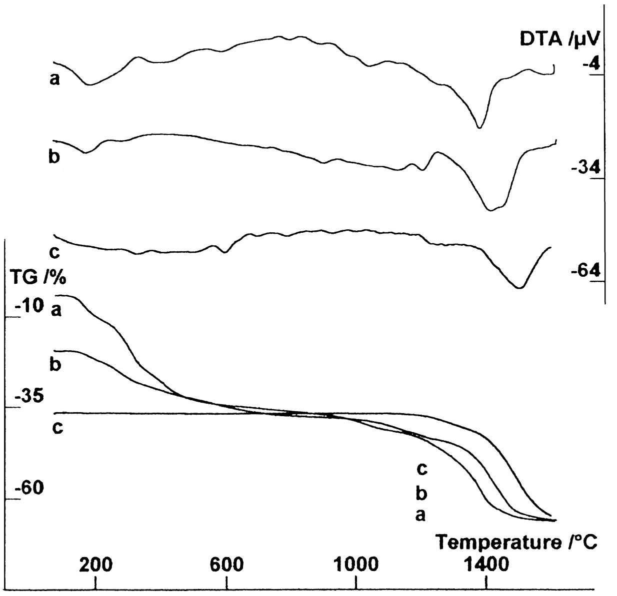


Fig. 1. TG and DTA curves of (a) titanium alkoxide/carbonaceous hydrogel, (b) rutile/carbonaceous hydrogel, (c) rutile/carbon black mixture. TG ordinate was normalized with respect to the Ti content of samples.

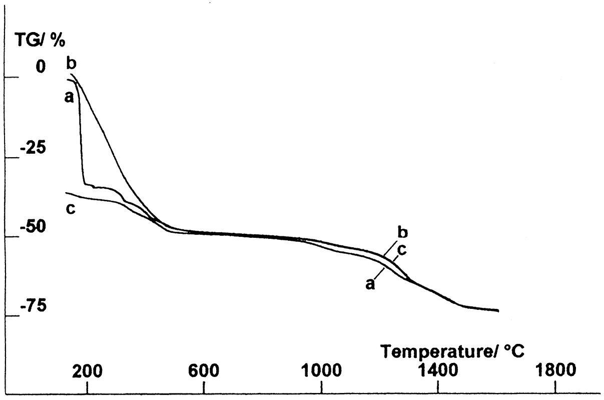


Fig. 2. TG diagrams of (a) titanium peroxide/saccharose hydrogel, (b) titanium acetate/saccharose organogel, (c) titanium glycolate/ethyl acetoacetate organogel. TG ordinate was normalized with respect to the Ti content of samples.

the alkoxide/carbonaceous gel at 800°C in Fig. 3(a) is an example for this pyrolysis stage, suggesting an intimate and uniform association of TiO_2 and carbon. The carbon content of all gels pyrolyzed at 800°C, amounts to a value of ~31 wt% which agrees with the stoichiometry for the TiC formation.

As demonstrated by XRD, anatase begins to transform into the rutile phase at 800–900°C in the case of hydrogels [e.g.Fig. 3(b)]. XRD as well as TG analyses (see. below) show that the carbothermal reduction immediately begins following this phase transformation. For the organogels no anatase → rutile transformation is observed within the carbon/oxide composite; the reduction starts from the anatase form. Table 1 summarizes the crystalline phases detected by XRD during the crystallization and carbothermal reduction processes.

3.3 Reduction sequence

The XRD results in Table 2 demonstrate a sequence of solid reaction products during the carbothermal reduction of the gel–systems which corresponds with the reduction sequence proposed recently:[22]

$$TiO_2 \rightarrow \text{Magneli phases} \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiO_xC_{1-x} \rightarrow TiC$$

The Magneli compound Ti_4O_7 (JCPDS-card 18-1402) is observable as first reduction product of the carbonaceous gel containing systems (Magneli phases higher than Ti_4O_7 have not been detected probably due to the relatively large heat treatment interval of 100°C and the high reactivity at the start of the reaction). Its XRD lines begin to emerge at temperatures lowering from 1200 to 900°C in the sequence rutile/carbon black to rutile/carbonaceous gel to the binary gels. Figure 3 gives the phases observed for the alkoxide/carbonaceous gel during the overall reduction process; the lines at 1000°C are those of Ti_4O_7. Only weak lines indicative of Magneli phases and γ-Ti_3O_5 (JCPDS-card 40-806) have been found for the saccharose containing systems at 1000°C. Strong lines of 8-Ti_3O_5, however, are found for the glycolate organogel at 1000°C.

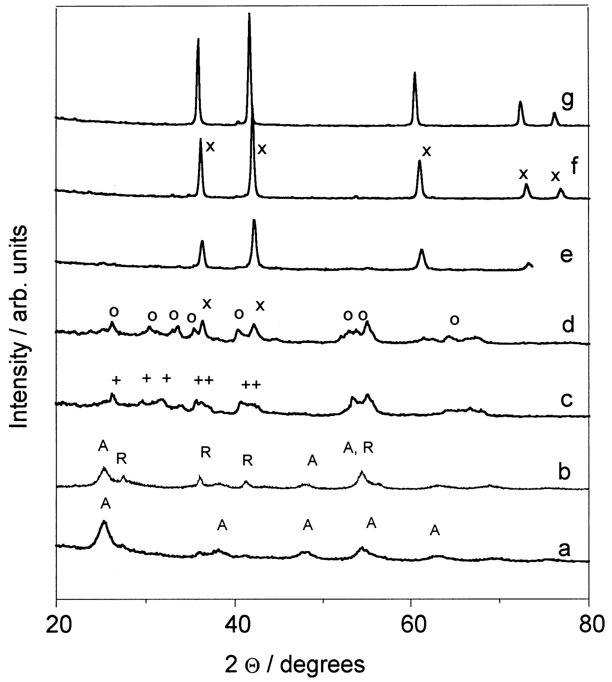


Fig. 3. XRD patterns of titanium alkoxide/carbonaceous gel heat treated under argon in the temperature range (a) 800°C to (g) 1400°C in 100°C intervals (A, anatase; R, rutile; +, Ti_4O_7; o, γTi_3O_5; x, titanium oxycarbide).

The XRD patterns at temperatures above 1000°C reveal different reduction kinetics for the systems studied. Formation of titanium oxycarbide occurs in the binary gels already at about 1100°C. The lines of its cubic structure are present together with those of γ-Ti_3O_5 and Ti_2O_3(JCPDS-card 10-63) at 1100°C. The alkoxide gel gives lines for γ-Ti_3O_5 and the oxycarbide at this temperature [Fig. 3(d)]. The patterns at 1200°C show that Ti_3O_5 has been completely reduced, and only weak Ti_2O_3 lines with intensities differing for the various gel systems are present (e.g. Figure 3).

The patterns at 1300°C show only carbide lines in all binary gels. For rutile/carbon black and rutile/carbonaceous gel, however, the lines of the suboxides α-Ti_3O_5 (JCPDS-card 11-217) and β-Ti_3O_5 (JCPDS-card 23-606) are simultaneously present with those of the oxycarbide at 1300–1400°C, but cubic oxycarbide is the only phase present above 1400°C. The shift of the temperature at which only the oxycarbide phase is present in the different systems reflects the higher reactivity of the binary gels compared to those with rutile as the starting compound (a better illustration of this temperature shift is given by the DTG curves in the next section).

In the high temperature region (1200–1600°C), the diffraction lines of the cubic oxycarbide phase become narrower and shift to lower 2θ with rising temperature, suggesting crystallite growth and increase of the lattice parameter. Table 3 gives lattice parameters and crystallite sizes determined by line broadening analysis of titanium oxycarbide obtained from alkoxide/carbonaceous gel heated at 1200–1500°C. The increase of the lattice parameter corresponds with a gradual substitution of oxygen by carbon in the oxycarbide lattice.[23]

3.4 Thermogravimetric analysis of the carbothermal reduction

The TG curves in Figs 1 and 2 monitor that the onset of the carbothermal reduction varies from ~870 to 1150°C for the different systems studied.

Table 2. Crystalline phases observed for binary gels at different annealing temperatures (*T*)

T *(°C)*	*Alkoxide/ Carbonaceous hydrogel*	*Peroxide/ saccharose hydrogel*	*Acetate/ saccharose organogel*	*Glycolate /ethyl acetoacetate organogel*
600	Anatase	(Anatase)	Amorphous	Amorphous
700	Anatase	Anatase	Anatase	Anatase
800	Anatase	Anatase + (Rutile)	Anatase	Anatase
900	Anatase + Rutile	Anatase + (Rutile)	Anatase + (Ti_4O_7)	Anatase + (Ti_4O_7)
1000	Ti_4O_7	Ti_3O_5 + (Ti_4O_7)	Ti_3O_5	Ti_3O_5
1100	Ti_3O_5 + (Oxycarbide)	Ti_2O_3 + (Ti_3O_5) + Oxycarbide	Ti_2O_3 + (Ti_3O_5) + Oxycarbide	Ti_2O_3 + (Ti_3O_5) + Oxycarbide
1200	Oxycarbide + (Ti_2O_3)	Oxycarbide + (Ti_2O_3)	Oxycarbide + (Ti_2O_3)	Oxycarbide + (Ti_2O_3)
1300	Oxycarbide	Oxycarbide	Oxycarbide	Oxycarbide

The highest reduction onset is observed for the rutile/carbon black mixture and the lowest for the binary gels. This lowering may be due to the more intimate mixing of the reactants in the gels. Furthermore, the carbothermal reduction obviously proceeds through three reaction steps, as shown by DTG curves (Fig. 4). Endothermic DTA peaks, not depicted here, correspond with the DTG minima in Fig. 4. Whereas the three peaks are well separated for the binary gels the two high-temperature peaks are widely merged for the two systems with rutile. A three-step mechanism has also been found recently for the reduction of rutile by different types of solid carbon, and was explained with the intermediate formation of low titanium oxides and oxycarbides.[24]

The starting temperatures of the three reduction steps determined from the DTG and DTA curves are listed in Table 4 for all systems. The determination of the onset of reduction is based on a thermogravimetric determination of the mass of TiO_2 by total oxidation of the carbothermal reaction products. Two major points emerge from the temperatures in Table 4 and the intensities of the DTG minima. In the sequence rutile/carbon black to rutile/carbonaceous gel to binary gels the temperatures of the first and second reduction steps are lowered; the most significant lowering is observed for the first reduction step. Although no temperature differences are recognizable from Table 4 for the binary gels, the second DTG peak is more intensive for the saccharose containing gels than for the other systems, showing a higher reactivity of the saccharose derived coke. Secondly, in comparing the thermogravimetric behaviour in the highest temperature range, no striking differences are found for the systems studied. Merely for the rutile/carbon black mixture the third reduction peak is shifted to higher temperature.

According to the XRD results (Table 2) the lowest DTG peak is attributable to the first reduction step leading to Ti_4O_7 and Ti_3O_5 in correspondence with the findings in Ref. 24 (a shift to somewhat lower temperatures for the XRD data may be due to the longer holding times during the oven experiments). Ti_2O_3 and oxycarbide but no Ti_3O_5 are present for the binary gels after the second DTG peak. According to the XRD data this

Table 3. Lattice parameter (*a*) and crystallite size (*d*) of titanium oxycarbide produced from titanium alkoxide/carbonaceous gel by annealing at different temperatures (*T*)

T(°C)	a(*nm*)	d(*nm*)
1200	0·4278	18
1300	0·4293	25
1400	0·4319	40
1500	0·4320	44

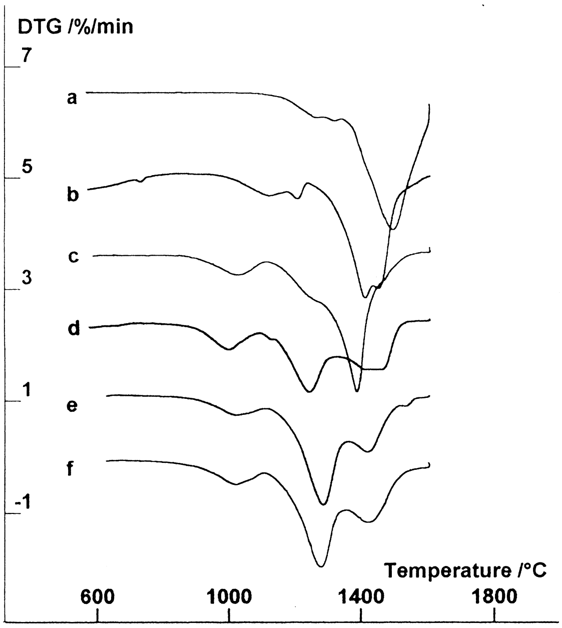


Fig. 4. DTG curves of (a) rutile/carbon black, (b) rutile/ carbonaceous gel, (c) titanium alkoxide/carbonaceous hydrogel, (d) titanium peroxide/saccharose hydrogel, (e) titanium acetate/saccharose organogel, (f) titanium glycolate/ethyl acetoacetate organogel. DTG ordinate was normalized with respect to the Ti content of samples.

Table 4. Temperatures (°C) of the beginning of the three reduction steps for the different titania systems

System	*1st step*	*2nd step*	*3rd step*
Rutile/carbon black	1150	1280	1380
Rutile/carbonaceous hydrogel	980	1200	1300
Alkoxide/carbonaceous hydrogel	870	1160	1300
Peroxide/saccharose hydrogel	870	1160	1300
Acetate/saccharose organogel	870	1160	1300
Glycolate/ethyl acetoacetate gel	870	1160	1300

reduction step proceeds in a narrow temperature range (1100–1200°C). Lastly, the peak at the highest temperature can be attributed to the substitution of O by C in the oxycarbide which proceeds with an increase of the lattice parameter (Table 3). For the two systems with rutile no Ti_2O_3 is observed, probably due to the relatively wide heating interval of 100°C and the merging of the two high-temperature peaks. The splitting of the two high-temperature peaks for the binary gels is discussed in section 3.6.

3.5 Pore generation during the heat treatment

Nitrogen adsorption measurement demonstrates that the alkoxide/carbonaceous gel is porous after heating at 200°C (BET surface area 180 $m^2 g^{-1}$). Stepwise pyrolysis reduces the surface area (300°C: 153, and 400°C: 118 $m^2 g^{-1}$) up to a minimum of 110 $m^2 g^{-1}$ at 500°C. Temperature increase up to 600°C newly increases the specific surface area.

All other gel systems are non-porous at temperatures <600°C. Pore generation starts in these xerogels between 600 and 700°C and leads to considerable BET surface areas already at 700 and 800°C. Figures 5–7 show some typical isotherms and Table 5 summarizes specific surface areas at different temperatures. The change of the shapes of the isotherms and the variations of the surface areas reflect the structural and chemical transformations during the heat treatment processes.

The shape of the isotherm for the alkoxide gel at 600°C depicted in (a) is characteristic for this gel for a wide temperature range (300–1300°C). The broad hysteresis loops indicate the presence of a high portion of mesoporosity, although the isotherm type is difficult to interpret. The mesoporosity of this gel in the pyrolysis range up to $\sim$600°C is probably associated with the titania component in the gel because neither the rutile/carbonaceous gel nor the pure carbonaceous gel produce any porous materials in this temperature range. The observed porosity, however, parallels to the findings with a silica/carbonaceous gel.[25] Controlled hydrolysis of silicon and titanium alkoxides is a widely used technique to prepare mesoporous silica or titania. Here, a porous diphasic C/TiO_2 material is formed when a carbon precursor is used which does not melt during pyrolysis, as the carbonaceous gel. On the other hand, in the presence of a meltable compound (saccharose) no porosity is produced upon pyrolysis lower than 600°C. Presumably, the meltable compound fills the pores or pore entrances of the oxide network. In this case, however, a material of a higher degree of densification is obtained after pyrolysis.

The generation of porosity in the saccharose and ethylene glycol containing xerogels at 600–700°C and the increase of porosity in the alkoxide/carbonaceous gel at 500–600°C may be ascribed to the crystallization of anatase; no thermogravimetric mass loss is observable in the corresponding temperature ranges. The isotherm of the saccharose hydrogel after annealing at 800°C is shown in Fig. 6(a) and that of the glycolate gel at 700°C in Fig. 7(a). Both can be classified as Type I isotherms revealing substantial microporosity. The determined BET values are at 200–300 $m^2 g^{-1}$. Analysis of the *t*-plot functions for the glycolate gel shows that these values are nearly completely associated with micropores at 700–800°C. Presumably, structural reorganization creates micropores during crystallization. This is different for the alkoxide/carbonaceous gel, where the additionally produced porosity does not alter the shape of the isotherm.

The adsorption behaviour changes through the three carbothermal reduction steps in a characteristic way. Temperature increase up to the onset of the reduction produces new isotherm types which are depicted for the 1000°C heated saccharose and glycolate gels in Figs 6(b) and 7(b). Their shapes are characteristic for Type IV isotherms, and the hysteresis loops can be classified as H4 loops. The broad hysteresis loops indicate the presence of mesoporosity in addition to the microporosity. The specific surface areas first increase during the carbothermal reduction, and after passing through a maximum at 1200–1300°C they decrease. The maximum coincides with the second reduction peak found with DTG experiments. The BET values for the alkoxide/carbonaceous gel (Table 5) also reveal a maximum which coincides with the first DTG peak (Fig. 4). The surface areas of the gels during the reduction stages are likely associated with mesopores; the microporosity of the glycolate gel is lower than for the 700–800°C range (Table 5). The pores are supposed to be formed by the expulsion of chemically generated CO throughout the carbothermal reduction. On the other hand, with rising temperature porosity may decrease caused by crystal growth and shrinkage of unreacted material, mostly the carbon matrix.

During the third reduction minima in the DTG curves the BET values continuously decrease, and the hysteresis loops more or less approach the type

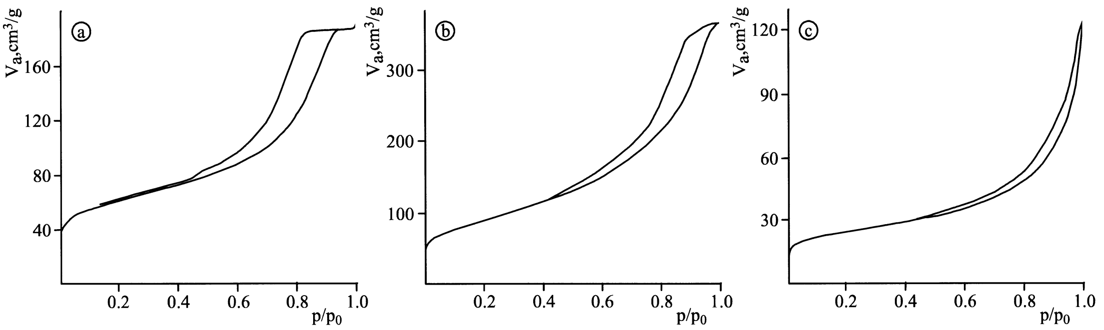


Fig. 5. Nitrogen adsorption isotherms of titanium alkoxide/carbonaceous hydrogel annealed at (a) 600°C, (b) 1300°C, and (c) 1500°C.

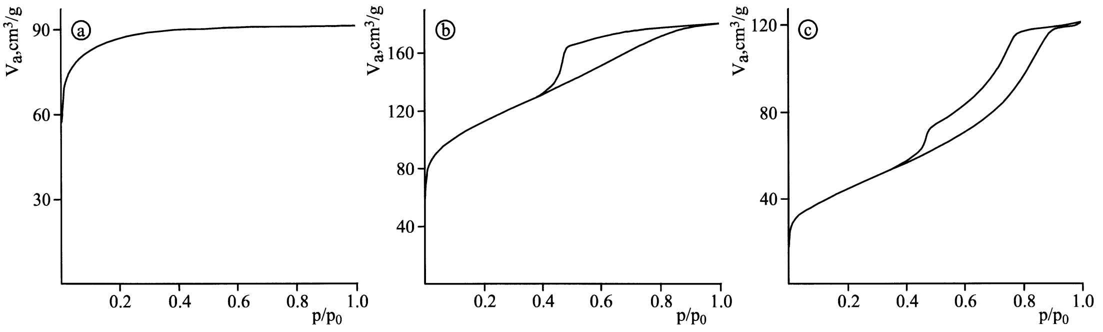


Fig. 6. Nitrogen adsorption isotherms of titanium peroxide/saccharose hydrogel annealed at (a) 800°C, (b) 1000°C, and (c) 1500°C.

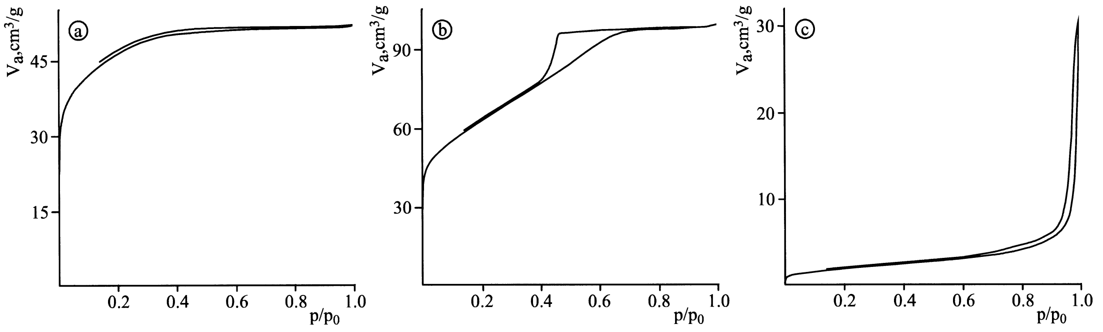


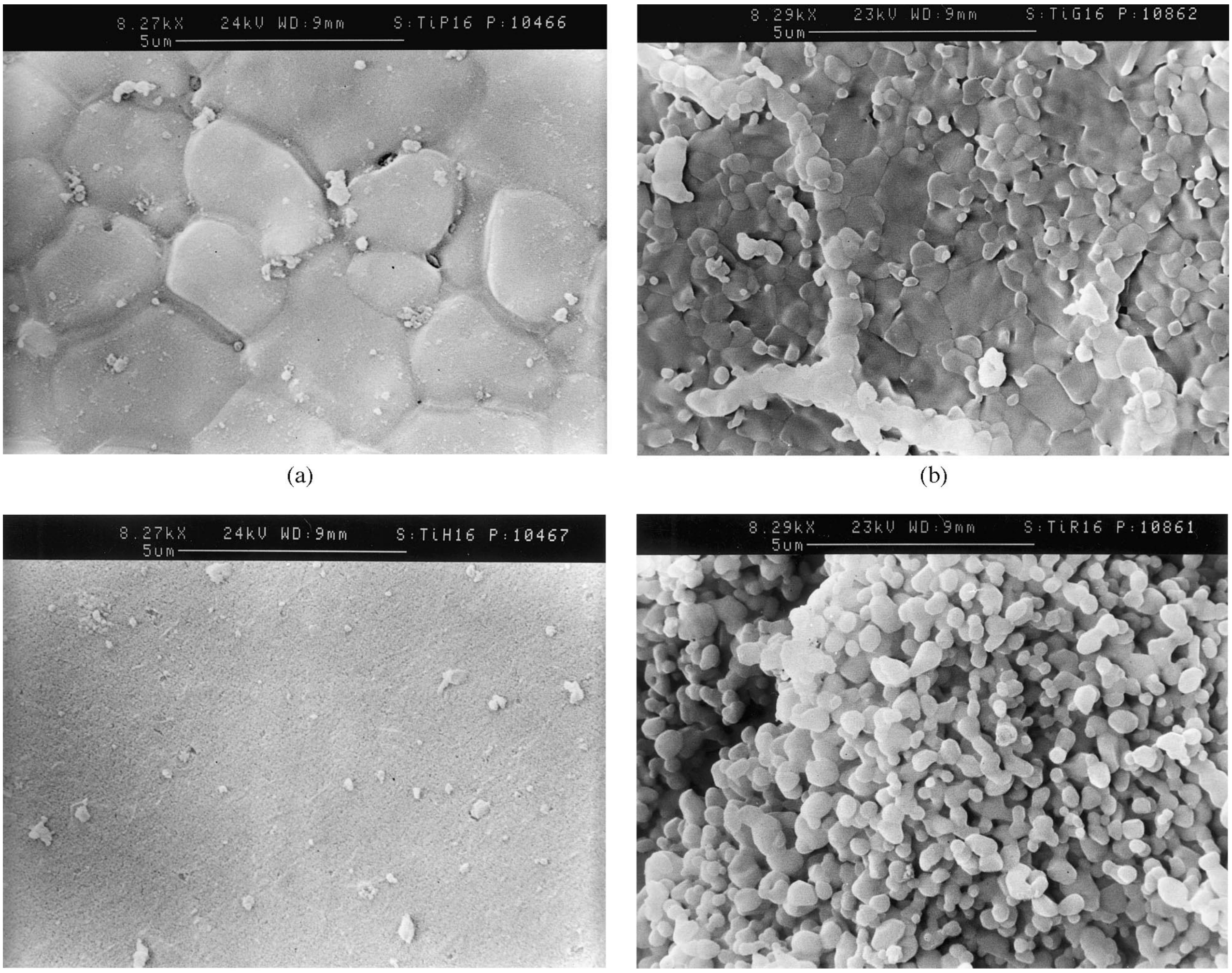
Fig. 7. Nitrogen adsorption isotherms of titanium glycolate/ethyl acetoacetate organogel annealed at (a) 700°C, (b) 1000°C, and (c) 1500°C.

Table 5. BET and micropore surface areas of binary gels at different annealing temperatures (*T*)

T *(°C)*	*Alkoxide/ carbonaceous hydrogel*	*Peroxide /saccharose hydrogel*	*Acetate/ saccharose organogel*	*Glycolate/ethyl acetoacetate organogel*	
	BET ($m^2 g^{-1}$)	*BET ($m^2 g^{-1}$)*	*BET ($m^2 g^{-1}$)*	*BET ($m^2 g^{-1}$)*	*Micropore ($m^2 g^{-1}$)*
600	178	3	151	57	56
700	254	306	212	166	165
800	260	314	227	191	190
900	339	318	245	194	45
1000	316	347	287	224	54
1100	335	390	320	253	50
1200	359	415	348	270	36
1300	322	321	373	264	20
1400	95	204	194	41	3
1500	25	158	159	7	1·2
1600	8	110	136	7	0·6

Table 6. Chemical composition of $TiC_xO_yN_z$ obtained at 1600°C

Gel type	C_{total} (wt−%)	C_{bond} (wt−%)	O (wt−%)	N (wt−%)	C_x	O_y	N_z
Rutile/carbonaceous hydrogel	19·2	17·58	2·44	0·61	0·88	0·09	0·03
Titanium alkoxide/ carbonaceous hydrogel	19·1	17·92	1·22	1·12	0·91	0·05	0·04
Titanium peroxide/ saccharose hydrogel	24·6	15·73	2·36	0·20	0·86	0·10	0·01
Titanium acetate/ saccharose organogel	27·5	15·80	1·19	0·29	0·89	0·05	0·01
Titanium glycolate/ethyl acetoacetate organogel	16·2	15·18	3·41	0·99	0·76	0·13	0·04



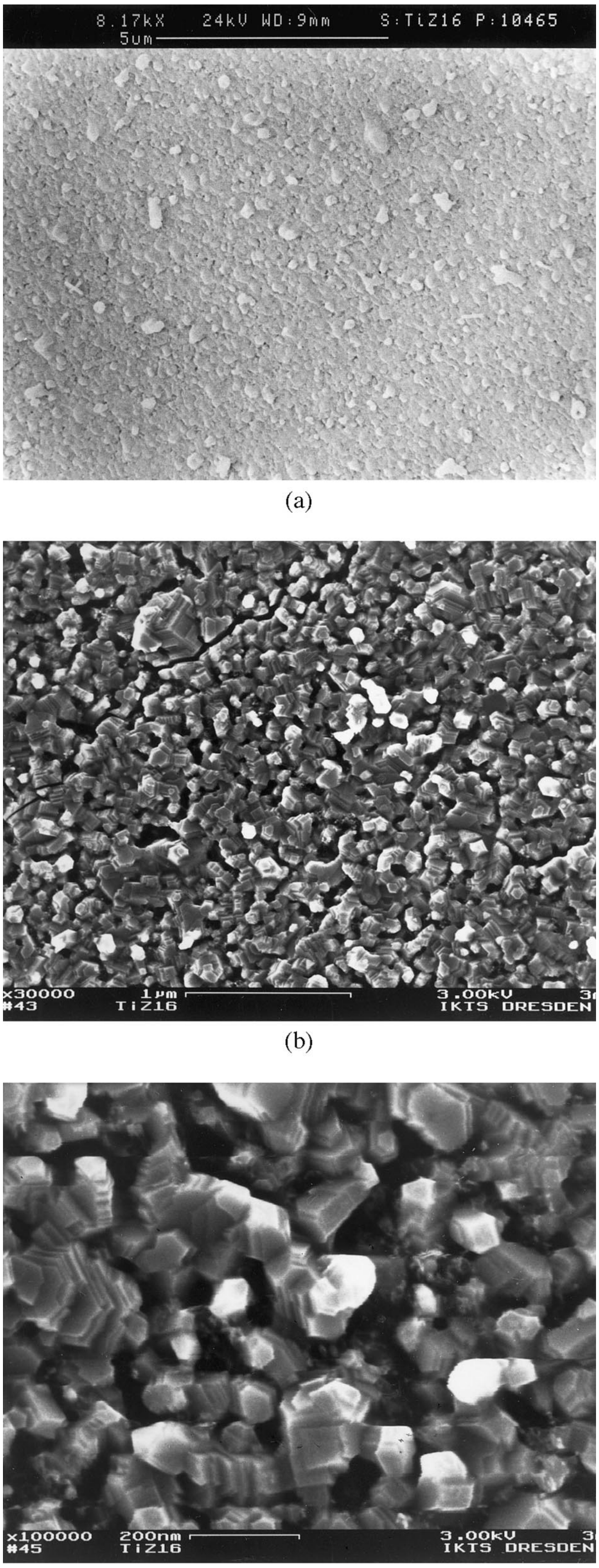
(a) (b)

(c) (d)

Fig. 8. Electron micrographs of surfaces of (a) the alkoxide/ carbonaceous hydrogel, (b) glycolate/ethyl acetoacetate organogel, (c) peroxide/saccharose hydrogel, and (d) rutile/carbonaceous hydrogel, all reacted at 1600°C.

H3 which is indicative of an aggregate or agglomerate structure. This approach is more distinct for the glycolate and the alkoxide gel at 1500°C [Figs 5(c) and 7(c)]. The shapes of the isotherms of the saccharose containing gels, however, are more indicative of incomplete reduction reactions [Fig. 6(c)]. It is thought that the relative high surface area at 1500°C is attributable to the presence of unreacted carbon.

Table 6 comprises the results of the chemical analysis of the non-metals for the final products obtained at 1600°C. The values prove the reaction products as oxycarbides with oxygen contents varying from 1·19 to 3·41 wt%. The low nitrogen content probably stems from the atmosphere in the furnace. For the saccharose containing gels the content of free carbon is relatively high, explaining the high surface areas.



(a)

(b)

(c)

Fig. 9. Electron micrographs of different magnification (a)–(c) of titanium acetate/saccharose organogel after heat treatment at 1600°C.

Figures 8 and 9 show SEM micrographs of the gels reacted at 1600°C. After heat treatment all final products look like large broken gel parts. SEM images of their surfaces show that they consist of agglomerated individual grains. The order of grain size is alkoxide/carbonaceous gel > glycolate/ethyl acetoacetate organogel > acetate/saccharose organogel > peroxide/saccharose hydrogel. The powder obtained from the rutile/carbonaceous gel shows a different structure. Relatively fine grains exist in a loosely agglomerated structure.Figure 9(a)–(c) give the real crystallite structure of the reaction product at 1600°C from the acetate/saccharose organogel at different magnifications. The images at the higher magnification show that fine crystallites of the oxycarbide have formed a sintered cascade-like structure with entrances into the pore system. Some grains exhibit dislocations. At the higher magnification free carbon particles are also visible.

3.6 Effect of *in situ* generated carbon on crystallization behaviour and reduction kinetics

Syntheses of titanium carbide and oxycarbide by carbothermal reactions from gel precursors differ from conventional oxide/carbon mixtures by the appearance of the additional processes of pyrolysis and crystallization before the onset of the carbothermal reduction itself. Upon pyrolysis first a homogeneous mixture of the reactants carbon and amorphous TiO_2 is formed. It is assumed that in this pyrolysis stage amorphous titania is constrained in a rigid carbon matrix. The carbon matrix prevents crystallization into anatase over a wide temperature range as indicated by X-ray diffraction and porosity measurement. For the denser organogels the crystallization temperature is higher than for the hydrogels. Moreover, the carbon matrix opposes the transformation of anatase to rutile up to the temperature where the reduction processes start, likely promoted by the phase transformation. Clearly, the gel system with rutile as starting material reveals the highest temperature for the onset of the reduction.

The studies show that dispersion and structure of carbon in the pyrolysed material influence the reaction kinetics of the carbothermal reduction. The increasing intimity of mixing in the sequence rutile/carbon black to rutile/carbonaceous gel and to the alkoxide/carbonaceous hydrogel effects a gradual decrease of the onset temperatures for the first reduction steps (Table 4). For further clarifying the role of *in situ* generated carbon in the binary gel, the quantity of carbonaceous gel in the binary hydrogel was varied. The crystallite sizes and BET surface areas of four alkoxide/carbonaceous hydrogels A–D with different contents of carbonaceous gel (see Section 2.1), and consequently of carbon, after heating at 1500°C are listed in Table 1. The crystallite sizes decrease and the BET values increase with increasing carbon content, showing a crystallization inhibition by excess carbon.

Comparing the alkoxide/carbonaceous gel with the other binary gels throughout the reduction steps, a more extended reaction in the second step at 1200°C is apparent for the latter types. The intensities of the peaks are higher, and XRD demonstrates the presence of Ti_2O_3 contrary to Ti_3O_5 for the alkoxide/carbonaceous gel. The faster reaction in the saccharose and glycolate systems may be due to a higher reactivity of the derived cokes in comparison with the coke formed from the carbonaceous gel. As already reported[26,27] the reactivity of carbon in carburization reactions is higher the farther away its structure is from that of graphite. It is likely that carbonaceous gel prepared from pitch precursors leads upon pyrolysis to a coke consisting mainly of aromatic, pregraphitic structural units. On the other hand, the coke formed during saccharose pyrolysis has a higher portion of sp^3 hybrided and cross-linked carbon, consequently, it is of a lower degree of graphitization.

The accelerating effect of the *in situ* generated carbon on the formation of lower oxides during the first reduction steps, however, does not hold for the formation of oxycarbides and carbides with high carbon content until high temperatures. The splitting between the second and third DTG peak (Fig. 4) is indicative of a delayed reduction reaction. Such splitting of the overall reduction reaction has also been found for the carburization of gel-derived NbC and TaC precursors.[12] It is assumed that the slow-down of the reaction rate is due to an interruption of the intimate contact of the reactants by consumption of carbon and the generation of pores during the carbothermal processes (see Section 3.5). Then the crystals of the oxides are allowed to grow and to agglomerate. On the other hand, both the diffusion of carbon into the crystal structure and the CO/CO_2 transport mechanism are delayed by this crystal growth, and Ti_2O_3 is detected when a distinct splitting of the second and third DTG peak is obseved. Thermodynamic calculations for the formation of titanium carbide and oxycarbides have proved that the differences in the free energies between Ti_2O_3 and oxycarbide with a relatively high O content is much smaller than the difference between Ti_2O_3 and Ti_3O_5.[28] Therefore the possibility to detect Ti_2O_3 is favoured by a delayed reaction kinetics which prolongs the reduction into oxycarbide. Higher thermal energy is then required to complete the reduction. The lack of intimate contact of the reactants caused during the initial reduction steps probably entails that the final step—the substitution of O by C in the oxycarbide—proceeds nearly at the same temperature as observed for the oxide/carbon black mixture.

4 Conclusion

The current work demonstrates that binary inorganic/organic gels can be prepared by hydrolysis of titanium alkoxide in the presence of soluble, pyrolyzable organic compounds and complexing additives. Upon pyrolysis up to 600–800°C, the gels transform into intimate mixtures of solid carbon and nanometer sized anatase. The pyrolyzed xerogels can serve as easily synthesized precursors to titanium oxycarbide and carbide. The synthesis route to the binary gels can be used to control the elemental composition in the annealed products.

Four different binary gels have been synthesized, and their thermal behaviour has been compared with a rutile/carbon black mixture and a seeded gel in which crystalline TiO_2 (rutile) was dispersed in a carbonaceous hydrogel. Investigation of the carbothermal processes using TG/DTA, XRD and nitrogen adsorption has established the reaction to proceed through three consecutive steps: the reduction of TiO_2 to the lower oxides Ti_4O_7 and Ti_3O_5, the formation of Ti_2O_3 and TiO_xC_{1-x}, and finally the gradual substitution of O by C in the oxycarbide. In the sequence rutile/carbon black to rutile/carbonaceous gel to binary gels the onset temperature of the initial carbothermal reaction steps are decreased, showing a highly promoted reaction kinetics by intimate mixing of the reactants in the binary gels. The promoted reaction kinetics leads to homogeneous nucleation in the first reduction steps. The final temperature for complete carburization, however, is only insignificantly reduced. This may be due to an interruption of the intimate contact of the reactants by pore generation during the initial steps.

Heat treatment transforms the binary xerogels into microporous and mesoporous intermediates and fine-grained final products. The consecutive processes of crystallization, chemical reactions and crystal growth control the pore systems. The porous composites and the fine carbide powders may be used as catalysts, catalyst supports or as materials for the preparation of ceramic composites.

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