JOURNAL OF MATERIALS SCIENCE 33 (1998) 713–722

Preparation of molybdenum and tungsten carbides from solution derived precursors

H. PREISS, B. MEYER, C. OLSCHEWSKI
TU Bergakademie Freiberg, Institut für Energieverfahrenstechnik und Chemieingenieurwesen, 09596 Freiberg, Germany

Synthesis principles have been developed for the preparation of solution derived precursors that can be selectively converted to desired refractory materials, as powders, fibres or thick films. The precursors are prepared from aqueous or ethylene glycol solutions containing a pyrolysable organic compound (carbonaceous gel or saccharose) and a soluble molybdenum or tungsten compound (peroxo acid or ethylene glycolate). The concentrated solutions exhibit rheological properties that allow fibre drawing and production of thick films. The sequence of the high temperature reactions – pyrolysis, reduction, carburization – was investigated by thermal gravimetric analysis (TGA), X-ray analysis and nitrogen adsorption. Because of the high homogeneity of the reactants, carbon and transition metal suboxides in the pyrolysed precursors, the observed carburization temperatures (800–1200 °C) are lower than those used industrially. Most of the intermediate and final products – carbon/oxide composites, Mo(C, O), Mo_2C, W_2C, and WC – are materials of a high Brunauer–Emmett–Teller (BET) surface area (50–200 $m^2 g^{-1}$). © *1998 Chapman & Hall*

1. Introduction

The conventional industrial production of molybdenum and tungsten carbides is a powder metallurgical process starting from the corresponding oxides or tungstic acid. The oxides are initially reduced by hydrogen to metal powders. The metals are then blended with carbon powders, mostly carbon black, and carburized at high temperatures (1500–2000 °C) to generate the carbides. This process, which is very energy intensive because of the high temperatures, leads to carbides quite usable for the production of cutting tool components. But their increasing use in catalysis and ceramics requires materials of a high specific surface area. Many synthesis procedures for the preparation of transition metal carbides of fine particles and a high surface area have been reported recently. Reviewing the synthesis work, the requirement of low-temperature treatments that minimize sintering during the preparation is stated. Thus, low-temperature processes in a like manner lead to high surface area materials and economize on energy costs. Gas phase reactions, gas–solid reactions, and solid state reactions starting from precursors with an intimate mixture of the reactants are the mostly used preparation techniques.

Earlier published methods for the production of molybdenum and tungsten carbides of a high surface area (10–40 $m^2 g^{-1}$) involved the carburization of the corresponding oxides with CO [1–3]. The reaction temperature could be substantially lowered in comparison with the metallurgical solid state process. The produced carbides, however, were not catalytically active because their surfaces were covered with polymeric carbon. This carbon stems from the decomposition of CO. A reduced covering and a higher catalytic activity was achieved with CO/H_2 mixtures [3]. Better results could be achieved using a reactive CH_4/H_2 mixture to transform molybdenum and tungsten oxides or nitrides into high surface area carbides (100–200 $m^2 g^{-1}$) [4, 5]. The used temperature-programmed technique allows an independent control of oxygen removal and carburization rates; the pore structure of the materials, however, is not controllable. Unreacted oxygen and deposited carbon may inhibit catalytic activity, both can be widely removed by surface cleaning with hydrogen [6, 7]. The problems involved with the carbon deposition are avoided by inverting the preparation technique [8, 9]. The method of Ledoux involves the vaporization of an oxidic gas (MoO_3, WO_2, SiO) which reacts with a solid activated carbon. Surface areas of ~150 $m^2 g^{-1}$ are generated by a "memory" of the porous structure of the starting solid carbon.

The use of designed organometallic compounds as precursors for solid-state reactions is an alternative method of producing refractory materials. An example is the formation of tungsten carbides from tungsten alkyne complexes [10]. The advantages of this technique are that the organometallics may be shaped, and that the conversion into the carbides proceeds at a moderate temperature. Disadvantages are the high costs of the precursor preparation and the uncontrollable stoichiometry of the carbides produced. The formation of submicrometre tungsten carbide by the pyrolysis of polymer precursors has also attracted wide interest. The polymers were prepared by reacting metal halides, alkoxides or complex compounds with a carbohydrate [11] or a phenolic resin [12] as precipitates in a volatile organic solvent. The low surface areas of the materials produced this way may be because of the fact that no uniform mixing of the reactants on a molecular or even atomic level had been attained.

In this work, we report on synthetic approaches to molybdenum and tungsten carbides where the required composition for the precursor is formed in a solution. High homogeneity of the precursor is achieved by dissolving (1) a commercially available molybdenum or tungsten compound, and (2) a pyrolysable carbon compound in a usual solvent, as aqueous hydrogen peroxide (H_2O_2) or ethylene glycol. The solvent is then vaporized without giving rise to a precipitation reaction; sometimes the solutions (sols) pass through a gel state during concentrating. MoO_3, molybdic or tungstic acid are used as the starting transition metal compounds, and carbonaceous gels [13] or saccharose are the respective pyrolysable carbon compounds. The precursors are heated under an inert atmosphere up to 800–1200 °C to form the carbides. The reaction sequences of the carbothermal processes are followed by thermogravimetric analysis (TGA), X-ray diffraction and N_2 adsorption measurements.

Apart from the considerations mentioned above, this technique is not expensive because it requires no apparatus and no risky organic solvents. The possibility of controlling the viscosity of the solutions and sols allows the technique to be used for the production not only of powders but also of thick films and fibres.

2. Experimental procedure

2.1. Sample preparation

2.1.1. Molybdenum peroxide derived precursors

MoO_3 (1.44 g; 0.01 mol) were suspended in 5 ml 30% aqueous H_2O_2 at room temperature. After 50 h, 5 ml distilled water were added, and the solution was decanted from the undissolved residue. The residue was digested with 1 ml 30% H_2O_2 at ~60 °C until it was dissolved. Then both solutions were combined and heated at ~80 °C in order to decompose excess H_2O_2 whilst the colour of the solution changed from yellow into orange. If the solvent is allowed to evaporate at room temperature, crystalline molybdenum peroxide hydrate [14] will precipitate from this solution. On the other hand, the orange solution was used as the starting solution for the preparation of the carbide precursors.

In order to prepare the molybdenum peroxide/carbonaceous gel precursor, a solution of 0.60 g of a dried carbonaceous gel and 0.60 g glycerol in 10 ml distilled water was added under stirring at room temperature to the starting "Mo solution" as prepared. Concentrating at ~80 °C led to a black gel. Subsequent drying at 120 °C led to fragments of the precursor. The carbonaceous gel of 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 [13] was prepared from a coal tar pitch.

The molybdenum peroxide/saccharose precursor was prepared by dissolving 1.02 g of saccharose in the starting "Mo solution". Upon heating at ~60 °C a blue solution was formed, showing that Mo^{6+} had been reduced to colloidal molybdenum blue. Evaporation of the solvent and subsequent drying at 120 °C led to blue precursor fragments.

2.1.2. Molybdenum ethylene glycolate derived precursors

Molybdic acid (1.69 g), which has an assay of 0.01 mol MoO_3, were dissolved in 10 ml ethylene glycol under heating at ~60 °C. Heating was carried on until the odour of ammonia could no longer be detected (the commercial molybdic acid contains ammonium molybdate). Then different quantities of saccharose (A, 0.10 g; B, 0.80 g; and C, 1.60 g) were added to prepare the precursor solutions A, B, and C in each case. The amount of saccharose for the precursor A has been chosen to adjust the carbon content necessary for the formation of almost stoichiometric Mo_2C during the high-temperature processes. The precursor solutions B and C have been used to study the occurrence of spinnability (i.e. the ability to form fibres) and the influence of excess carbon on the carburization reactions. After saccharose had dissolved upon warming, the solutions were concentrated at ~130 °C under stirring and tested for spinnability and film production. It has been proved that all precursor solutions are suitable for film production, but only the solutions B and C exhibited viscosities that allowed fibre drawing.

2.1.3. Tungsten peroxide derived precursors

Tungstic acid (2.55 g H_2WO_4), which has an assay of 0.01 mol WO_3, were suspended in 18 ml 10% aqueous hydrogen peroxide at room temperature. After 12 h, an acidic almost colourless solution had formed which was decanted from some undissolved residue. The residue was digested with 1 ml 30% H_2O_2 at ~60 °C. Then both solutions were combined and heated up to 80 °C to decompose excess H_2O_2. After most of the H_2O_2 had decomposed, an opalescent yellow solution (sol) had formed. If heating is carried on, the solution may turn into a yellow peroxide hydrate gel upon concentrating. However, in this case the yellow solution was used for the precursor preparation.

The tungsten peroxide/carbonaceous gel precursor was prepared by adding a solution of 0.70 g of the dried carbonaceous gel (see Ref. [13]) and 0.70 g glycerol in 10 ml distilled water to the yellow solution of the peroxotungstic acid. Then the mixed solution was concentrated at ~80 °C until it gelled. The gel was dried at room temperature and afterwards at 120 °C; thus fragments of a black precursor had formed.

To obtain a saccharose-containing precursor solution, 1.38 g saccharose were dissolved in the yellow peroxotungstic acid solution. The peroxotungstic acid/saccharose solution exhibited a remarkable stability under heating. Thus, it could be used for film preparation by immersing a substrate. Upon concentrating at ~80 °C, the solution transformed into a blue gel. The change of the colour is due to the reduction of W^{6+} to tungsten blue. The films and gel fragments were dried at 120 °C before the high-temperature treatment.

2.1.4. *Tungsten ethylene glycolate derived precursors*

Tungstic acid (2.55 g), which has an assay of 0.01 mol WO_3, and different quantities of saccharose (D, 1.40 g; E, 1.80 g; and F, 2.20 g) were in each case suspended in 10 ml ethylene glycol. Under stirring for approximately 3 h at 100 °C under reflux, the brown precursor solutions D–F were formed. Then the solutions were concentrated at ~130 °C up to a consistency which allowed for fibre drawing. Fibres were hand-drawn by extracting a glass rod from the viscous solutions at ~50 °C. It has been found that all precursor solutions were generally suitable for spinning; however, spinnability became better with rising quantity of saccharose in the solution. For powder production the viscous solutions were heated up to 190 °C, while fragments of the precursors were formed.

2.2. Heat treatment

The precursor fragments as well as the fibres and coated substrates were annealed in graphite boats using an alumina tube furnace (Carbolite Furnace Limited) at 400–1500 °C with 100 °C intervals in flowing argon ($20\,l\,h^{-1}$). The heating rate was adjusted to $10\,°C\,min^{-1}$ up to 1000 °C, and $5\,°C\,min^{-1}$ for 1000–1500 °C. The time for annealing at the maximum temperature was 1 h.

2.3. Characterization

The thermal behaviour of the pure peroxide hydrates in air, and that of the precursor materials in argon atmosphere, were studied by TGA using a Setaram TAG 24 thermo-analyser. In addition, TGA was conducted in air for some final heating products to study the oxidation behaviour of the carbides. The heating rate was $15\,°C\,min^{-1}$ in all cases. Conventional Fourier transform infrared spectroscopy and X-ray diffractometry (MoK_α) were used to record the i.r. spectra and X-ray diffractograms.

Measurements of nitrogen adsorption/desorption at 77 K were performed after drying and degassing the samples under vacuum for 3 h at 350 °C using a Micromeritics ASAP 2000 instrument. Brunauer–Emmett–Teller (BET) surface areas, and mesopore surface areas as well as pore size distributions using the BJH standard computational procedures, and *t*-plots (micropore surface areas) according to Harkins and Jura were calculated from the nitrogen isotherms. BET surface areas for some samples were additionally determined according to the method of Haul and Dümbgen [15] (simplified single point procedure).

Chemical analyses of carbon and nitrogen were performed using the CHN-Analyser EA 1110 (CE Instruments). Oxygen was determined with LECO TC-436.

3. Results and discussion

3.1. Precursor formation

3.1.1. *Peroxide derived precursors*

The solutions of MoO_3 and H_2WO_4 in aqueous hydrogen peroxide are yellow or pale yellow and acidic, showing that peroxo acids have been formed in the presence of excess H_2O_2. Although the structure of these peroxo acids is unknown, a substitution of oxygen by O–O groups in the anions is likely. After decomposing the excess H_2O_2, the colour of the solutions changes, mostly into orange, which may be due to condensation and polymerization reactions. It is well known that transition metal peroxo isoacids turn into their poly versions by condensation in the absence of free H_2O_2, on the other hand, excess of H_2O_2 degradates these polyacids [16, 17]. Here, it was found that under successive heating the polyacids transform finally into peroxide hydrates which are obtained either as a crystalline precipitate, in case of Mo, or as a gel (for W). The X-ray pattern of the crystalline Mo compound corresponds with that reported for H_2MoO_5 (JCPDS card 41-359). Fig. 1 shows the i.r. spectra for the crystalline molybdenum peroxide hydrate and the dried tungsten peroxide gel. A characteristic feature of these spectra is the band at about $850\,cm^{-1}$ which may be assigned to the stretching vibration of peroxo oxygens (O–O). This band is a common characteristic for transition metal peroxo compounds [18, 19]. In the i.r. spectrum reported for H_2MoO_5 by Segawa *et al.* [14] the O–O vibration at $842\,cm^{-1}$ has not been reported. Thermogravimetric

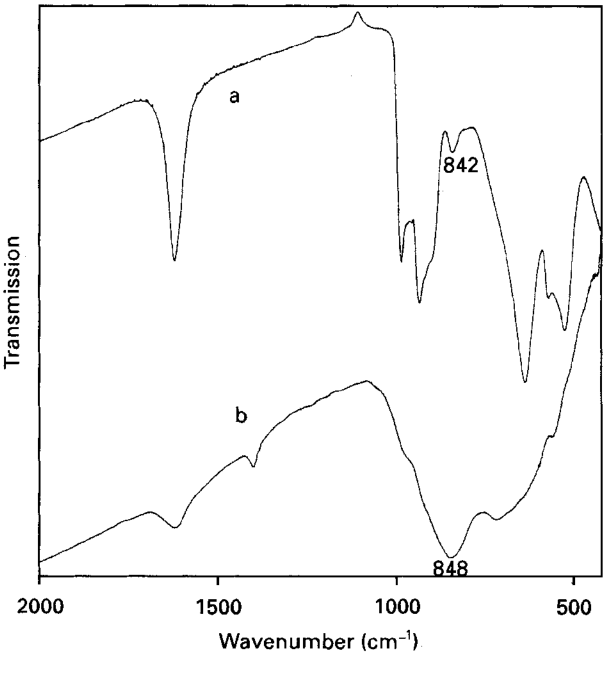

Figure 1 FTIR spectra of molybdenum peroxide hydrate (a) and tungsten peroxide hydrate (b).

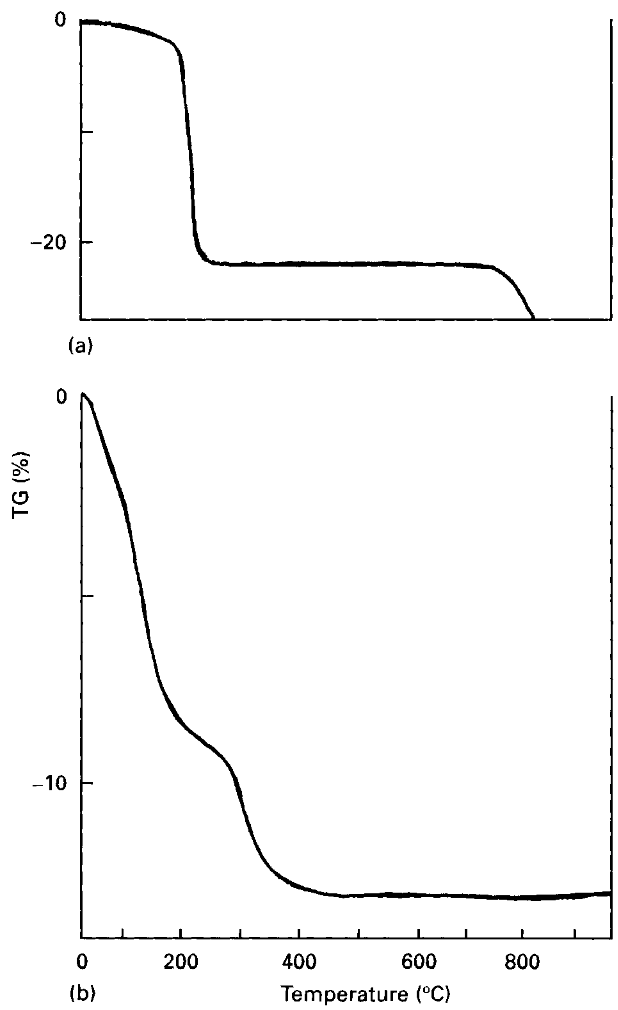

Figure 2 Thermogravimetric weight loss (TG) of molybdenum peroxide hydrate (a) and tungsten peroxide hydrate (b).

curves recorded for both peroxides up to ~ 800 °C are depicted in Fig. 2. The results show a two-step thermal decomposition reaction for the tungsten peroxide xerogel. The first step always beginning at room temperature is accompanied with a partial loss of water and hydrogen peroxide. The second step at ~330 °C may be due to a reorganization of the polyanion structure accompanied by the release of oxygen from the peroxo groups and of residual water. The X-ray pattern demonstrates that crystalline WO_3 in the monoclinic form (JCPDS card 43-1035) is present after this decomposition step. The TGA curve of the crystalline H_2MoO_5 exhibits only one decomposition step at ~220 °C. Using X-ray diffraction, the conversion of the peroxide hydrate into orthorhombic MoO_3 (JCPDS card 5-508) has been proven at this step. The weight loss of ~21% corresponds well with this conversion.

Upon addition of saccharose to the solutions of the peroxo acids, the solutions remain translucent and unchanged in colour. After some days at room temperature, the solutions transform into blue sols; under heating up to 50–80 °C, this transformation does not take longer than 1 h. The change of colour indicates the reduction processes to molybdenum or tungsten blue that are effected by saccharose.

When carbonaceous hydrosol is added to the solutions of the peroxo acids, black sols are formed which turn into gels upon concentrating. It is thought that gelling is caused by the carbonaceous component, see Ref. [20]. As demonstrated by X-ray analysis (see Section 3.3.), no reduction of Mo^{6+} and W^{6+} occurs in these sols.

3.1.2. Ethylene glycolate derived precursors

Molybdic acid dissolves in ethylene glycol at ~80 °C under evolution of NH_3 (commercial molybdic acid contains ammonium molybdate), and a colourless solution is formed at the very beginning. Although no structural investigations of the solution have been performed, the formation of molybdenum ethylene glycolates in this stage is likely; these molybdenum compounds have been previously synthesized from MoO_3 and ethylene glycol [21]. Because ethylene glycol is a reducing agent, the successive heating at ~80 °C renders the solution yellow and then brown. This change of colour is indicative of a stepwise reduction of molybdenum compounds leading finally to Mo^{5+} and Mo^{4+}. Synthesis of molybdenum and tungsten bronzes by refluxing MoO_3 and WO_3, respectively, with ethylene glycol have been recently reported [22]. Addition of saccharose to the solution darkens the colour of the solution, showing the strong reducing ability of this carbohydrate. It has been found that tungstic acid is completely soluble in ethylene glycol only in the presence of saccharose. The concentrated precursor solutions exhibit rheological properties that allow for fibre drawing. In order to obtain solid precursors for the study of pyrolysis and carbothermal reactions, the viscous solutions are heated up to 190 °C.

3.2. Thermal analysis

Typical TGA results for the molybdenum peroxide/carbonaceous gel, tungsten peroxide/carbonaceous gel and tungsten peroxide/saccharose precursor are given in Fig. 3. The TGA curves reveal two regions of strong weight loss: the first is indicative of the decomposition of the precursors, and the second of the carbothermal reactions. Decomposition begins in all systems almost immediately after heating and continues up to 400–500 °C. Most of the organic materials (carbonaceous gel, saccharose), the peroxides, and the molybdenum and tungsten blue decompose in this temperature range. The conversion of the carbonaceous gel into almost pure carbon has been studied recently, and it has been found that the main pyrolysis products CO_2, SO_2 and H_2O are evolved between 150 and 400 °C [20]. A mass loss which may be attributable to a step-wise formation of molybdenum or tungsten suboxides is superimposed to the pyrolysis of the carbonaceous gel and saccharose. Thus, the TGA curves do not run through a horizontal section before reaching the range of the carbothermal reduction to the carbides.

In the carbothermal reduction region, the TGA curve of tungsten peroxide/carbonaceous gel reveals two weight loss steps at ~850 and 1000 °C, showing that the high temperature reduction proceeds in at

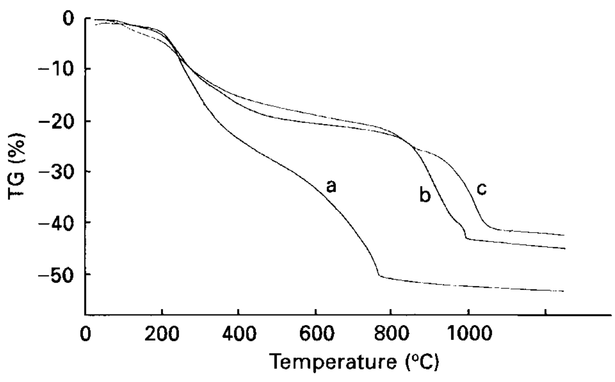

Figure 3 Thermogravimetric weight loss (TG) of molybdenum peroxide/carbonaceous gel (a), tungsten peroxide/saccharose (b) and tungsten peroxide/carbonaceous gel (c).

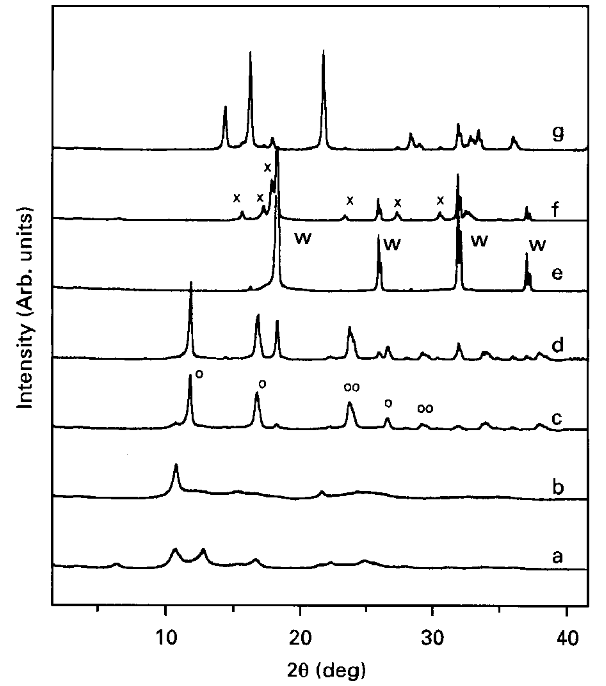

Figure 4 XRD patterns (MoK_α) of tungsten peroxide/carbonaceous gel at 500(a), 700(b), 800(c), 900(d), 1000(e), 1100(f) and 1200 °C (g); (○: WO_2; W: W metal; X: W_2C; at 1200 °C: only WC).

least two reactions. The end point of the reduction reaction, i.e. the point at which the TGA curve reaches a constant value is at about 1070 °C. To the contrary, the tungsten peroxide/saccharose system shows only one broad reduction step. The beginning of the carbothermal reduction at about 850 °C coincides with that for the carbonaceous gel system. The end of the reduction, however, is lowered by about 70 °C. The thermal behaviour of the tungsten glycolate/saccharose systems, although not shown in Fig. 3, is similar to that of tungsten peroxide/saccharose, revealing a reduction levelling out at ~1000 °C. At this temperature, WC is completely formed (see Section 3.3.). The contents of free and bonded carbon of the final products are between 6.5 and 6.9 wt %.

The lowering of the temperature for the carbide formation in the saccharose systems in comparison with the carbonaceous gel system may be explained by different carbon structures formed upon pyrolysis of both carbon precursors. It is well known that the reactivity of the carbon reactants in carbothermal reactions is generally the higher the further their structure is from that of graphite. A carbonaceous gel prepared from polyaromatic pitch precursors leads under pyrolysis to a coke consisting mainly of pregraphitic aromatic structural units. On the contrary, the carbon skeleton formed during saccharose pyrolysis has a high portion of sp^3 hybridized and cross-linked carbon atoms, and consequently, it is of a higher reactivity.

The TGA results of the molybdenum systems are different from those of the tungsten systems in that the carbothermal reduction proceeds at lower temperatures, and that the weight loss curve does not show a sharp step. Fig. 3 shows the TGA results of molybdenum peroxide/carbonaceous gel which is typical for all systems. The TGA curve gives no hints for intermediate products always observed in the reduction processes (e.g. MoO_2, molybdenum metal). The end point of the weight loss in all molybdenum systems is at about 780 °C.

3.3. Reaction sequence

All precursors as received after drying are X-ray amorphous. The crystallization of oxides in the precursor materials begins with the thermal treatment under argon in the range of 500–600 °C. In the tungsten peroxide/carbonaceous gel crystallization of WO_3 begins at about 500 °C. Fig. 4 shows the X-ray diffraction (XRD) patterns for this system after annealing at different temperatures. The broad reflections at 500 °C indicate the presence of nanocrystalline hexagonal WO_3 (JCPDS card 33-1387). This phase has a tunnel structure in which the WO_6 octahedra form hexagonal tunnels running along the *c*-axis. Heating at 600–700 °C effects reduction of this WO_3 form. Some broad reflections attributable to a suboxide of the composition $W_{24}O_{68}$ [23] (JCPDS card 36-103) are present at 700 °C. The structure of this oxide, which may be identical to that reported earlier [24], appears to resemble the tunnel compounds [25]. As supposed from the formation of tungsten blue sols (see Section 3.1.), no crystalline WO_3 is observed in the precursors prepared using saccharose, confirming a partial reduction to W^{5+} already in the solutions. The first crystalline oxide detectable from 500 °C for the saccharose systems is the $W_{24}O_{68}$ phase with crystallite sizes in the nanometre range as indicated by line broadening. The XRD lines of this oxide are present in all systems until lines of WO_2 begin to appear (a reduction sequence via other suboxides, e.g. $W_{18}O_{49}$, is likely but could not be detected with certainty because of the low intensity and broad width of the diffraction lines). WO_2 is the main reduction product for all the systems at 800 °C. With a temperature increase up to 900 °C, tungsten metal is formed in addition to WO_2 (see Fig. 4d). Pattern e in Fig. 4 demonstrates that the reduction to W metal is completed for the carbonaceous gel system at 1000 °C; only the W lines are observable. Carburization of W metal leads at 1100 °C (pattern f) to h.c.p. W_2C

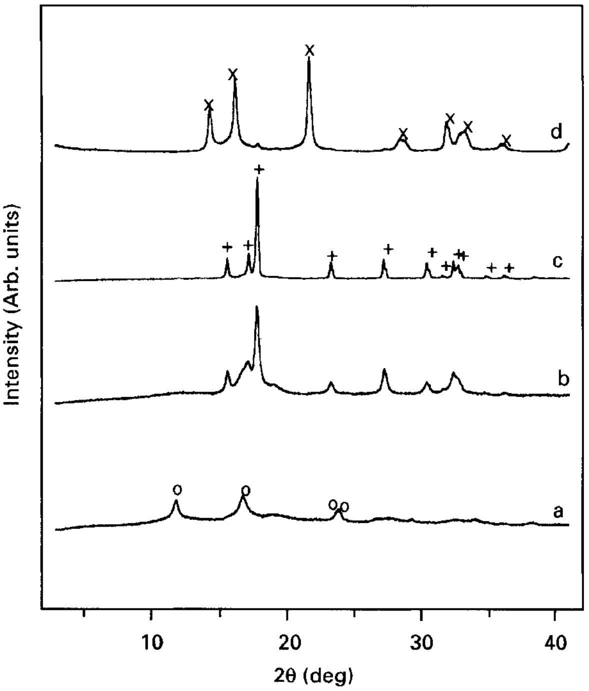

Figure 5 XRD patterns (MoK_α) of molybdenum peroxide/saccharose annealed at 700 °C (a), 800 °C (b), 1400 °C (c), and tungsten peroxide/saccharose at 1000 °C (d); (○: MoO_2; +: Mo_2C; X: WC).

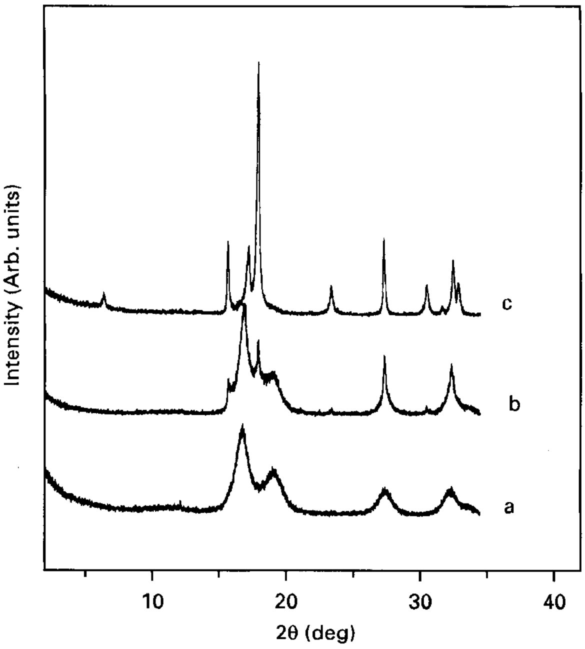

Figure 6 XRD patterns (MoK_α) of the molybdenum glycolate/saccharose precursors A (pattern c), B (pattern b), and C (pattern a) annealed at 1000 °C.

(JCPDS card 35-776) and finally to WC (JCPDS card 25-1047) at 1200 °C (pattern g). For all saccharose-containing systems the temperatures of the reduction and carburization processes are lowered; the pattern d in Fig. 5 shows the presence of only WC for tungsten peroxide/saccharose already at 1000 °C. Consequently, the X-ray results confirm the higher reactivity of the saccharose systems which may be caused by reduction reactions proceeding already in the solution stage, and to a higher reactivity of the saccharose coke.

The molybdenum precursors differ from the tungsten precursors during the heat treatment in that they remain amorphous up to 500 °C. MoO_2 (JCPDS card 32-671) is the first crystalline phase for the peroxide derived precursors after annealing at 600 °C. The reduction of MoO_2 as well as the carbide formation proceed in a narrow temperature range between 700 and 800 °C as can be concluded from X-ray diffraction. Fig. 5 shows the X-ray patterns of the molybdenum peroxide/saccharose system at 700, 800 and 1500 °C. Pattern b gives the lines of h.c.p. Mo_2C (JCPDS card 35-787) and additionally some broad peaks at 2θ ~17° and ~19° which may be attributable to a f.c.c. carbide structure, either an oxycarbide (JCPDS card 17-104), or MoC_{1-x} [26] which is reported to be a metastable form [27] ; recently a nearly stoichiometric f.c.c. MoC encapsulated by carbon nanotubes have also been found [28]. That no lines of intermediately formed Mo metal are found is not surprising because the carburization of the metal is a very fast reaction. After heating up to 1500 °C only the h.c.p. Mo_2C phase is present (pattern c in Fig. 5).

Heat treatment of the molybdenum glycolate/saccharose precursors A–C does not produce any crystalline oxide in our experiments. The precursors are X-ray amorphous up to 600 °C. Annealing at 700 °C leads either to a f.c.c. form (precursor B and C) or a mixture of this f.c.c. phase and h.c.p. Mo_2C (precursor A). Upon heating up to 1000 °C, the f.c.c. form may or may not transform into h.c.p. Mo_2C dependent on the carbon content in the products formed. It has been found that with precursor A the cubic phase transformed completely into hexagonal Mo_2C with a content of free and bonded carbon of 6.7 wt % (pattern c in Fig. 6). Precursor B leads at 1000 °C to a mixture of the cubic and the hexagonal phase with a total carbon content of 19.1 wt % (pattern b). Precursor C, however, gives a carbon content of 38.3 wt % and only broad lines of the cubic form (Fig. 6 pattern a).

In order to decide if the f.c.c. form is a Mo(O, C) oxycarbide or a metastable MoC_{1-x}, the oxygen content in the annealed precursor C was analysed with LECO TC-436. The oxygen content of 10.0 wt % at 1000 °C is in agreement with the existence of the oxycarbide. Considering the high carbon content of 38.3 wt %, the existence of an oxycarbide is surprising. Molybdenum oxycarbide has been hitherto prepared by pyrolysis of $Mo(CO)_6$ [29,30], which produces a high concentration of CO upon decomposition. Formation of the oxycarbide in our experiments may be explained with the absence of any porosity in the heat treated precursor materials (see Section 3.4) which inhibits that CO may be evolved. It is to be assumed that a high concentration of CO within the material stabilizes the oxycarbide. The line-broadening in Fig. 6a is indicative of the existence of nanometre-sized crystallites which are incorporated in a rigid carbon matrix at 1000 °C. Upon annealing at 1500 °C for 1 h, the cubic oxycarbide transforms into the h.c.p. Mo_2C, and the oxygen content reduces by up to 0.68 wt %, and the nitrogen content by up to 0.06 wt %.

In view of the occurrence of the oxycarbide, the two reaction sequences $MoO_2 \rightarrow Mo(O, C) \rightarrow Mo_2C$, and $MoO_2 \rightarrow Mo \rightarrow Mo_2C$ may be supposed for the carbothermal carbide formation in the solution derived precursors. The path via the oxycarbide seems to proceed under a high CO concentration.

3.4. Surface area and porosity

After drying at 120 and 190 °C, respectively, all solid precursors are poreless and do not show any noticeable BET surface area. During the pyrolysis of the carbon constituent (carbonaceous gel and saccharose), the precursors remain almost poreless up to 500 °C. A substantial increase of nitrogen adsorption is mostly observed above 500 °C. Curves of the BET values of tungsten peroxide/carbonaceous gel and tungsten peroxide/saccharose for the temperature range 500–1500 °C are depicted in Fig. 7. The surface areas of the other precursors are listed in Table I.

All precursors with exception of the molybdenum glycolate systems show a steep increase of surface area in the temperature range of the reduction processes, and after running through a maximum the surface areas decrease. The maxima of the BET values correlate with the weight loss steps in the TGA curves in Fig. 3, and with those points for which the X-ray analysis demonstrates the termination of the reduction and the beginning of the carburization (a shift to lower temperatures for some BET values may be explained by the longer holding times with the oven experiments). During the carburization reactions carbon is consumed, and the surface areas somewhat decrease. The BET values of the materials produced in the temperature range 1000–1200 °C are between 80 and 120 $m^2 g^{-1}$ showing that fine crystalline carbides are formed which may be advantageous candidates for heterogeneous catalysis. The further BET decrease above 1200 °C is probably caused by crystal growth and sintering of the carbide crystals forming polycrystalline aggregates.

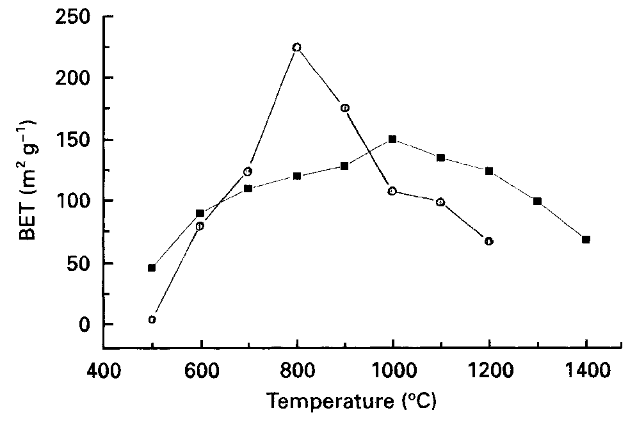

Figure 7 BET surface areas of annealing products of tungsten peroxide/carbonaceous gel (■) and tungsten peroxide/saccharose (○).

Isotherms of tungsten peroxide/carbonaceous gel after annealing at different temperatures are depicted in Fig. 8. The change of their shape with rising temperature is typical for all the systems studied; it was found also for ZrC, NbC and TaC synthesis from the respective precursors [31, 32]. For the 600 °C sample, the adsorption branch is nearly concave to the p/p_0 axis and approaches a limiting value at the highest p/p_0 value. No closure of the hysteresis loop is observed in the low pressure range. Both characteristics are indicative of a H4 hysteresis loop, and thus of the presence of microporosity. By using the *t*-plot method, a high portion of micropore area has been calculated (Table I). Since X-ray diffraction shows the appearance of crystalline WO_3 in the temperature range 500–600 °C, the microporosity may be associated with nucleation and crystallization phenomena. It is thought that migration processes and increase of density create cracks and voids with micropore widths in the rigid matrix. With temperature increase above 600 °C, the beginning of the carbothermal reduction leads to an expulsion of CO_2 and CO, and additional mesoporosity with pore diameters of 2–10 nm is generated. The isotherm for the 800 °C sample reveals

TABLE I BET, micropore area and pore diameter maxima of some tungsten and molybdenum precursor types at different annealing temperatures (T)

T (°C)	Mo			W		
	Peroxide/ carbonaceous gel BET ($m^2 g^{-1}$)	Peroxide/ saccharose BET ($m^2 g^{-1}$)	Glycolate/ saccharose A BET ($m^2 g^{-1}$)	Peroxide/carbonaceous gel		Glycolate/ saccharose D
				Micropore area ($m^2 g^{-1}$)	Pore diameter (nm)	BET ($m^2 g^{-1}$)
500		2				3
600	25	106		46	< 1	85
700	104	118	< 2			154
800	111	165	< 2	38	4.5	236
900	125	150	< 2	38	5.5	234
1000		150	< 2			94
1100	123	148	< 2	43	10–20	53
1200	120	111		18	10–40	33
1300	103	95				
1400				3	40–80	
1500	37					

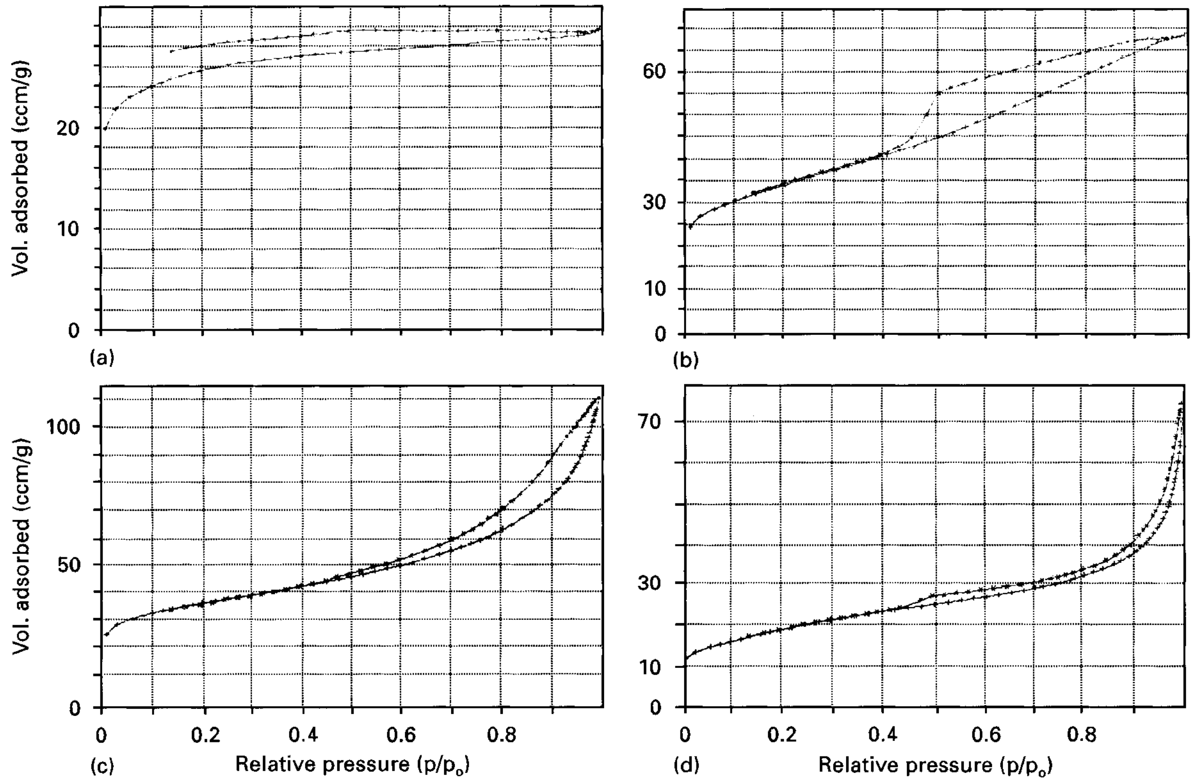

Figure 8 N_2 sorption isotherms of tungsten peroxide/carbonaceous gel annealed at 600 (a), 800 (b), 1100 (c) and 1400 °C (d).

a Type H2 hysteresis loop, which is attributable to capillary condensation in mesopores. This isotherm type is observable during the reduction stages for all the systems studied. Additionally, the micropore area is nearly constant in the reduction range; for tungsten peroxide/carbonaceous gel it decreases only when the temperature exceeds 1100 °C (Table I). Since unreacted carbon is yet present during the reduction range, it is suggested that the micropores and the mesopores between 2 and 10 nm are mainly associated with the presence of carbon. The consumption of carbon during the following carburization markedly changes the shape of the isotherms. The shape of the isotherm of tungsten peroxide/carbonaceous gel changes at 1100 °C, and the hysteresis loop approaches the Type H3 (Fig. 8c). Mesopores with diameters > 10 nm are additionally formed. At 1400 °C, the hysteresis loop is a typical H3 Type which is commonly observed with aggregates or agglomerates. This change of the isotherms demonstrates that the overall carbothermal reaction results in a product consisting of fine crystalline particles which are more or less joined together forming aggregates or agglomerates.

3.5. Oxidation behaviour

Contrary to the industrially produced molybdenum and tungsten carbides which are stable in air up to about 700 °C, the high surface area carbides become unstable at lower temperatures. They are slowly attacked even at room temperature. Recently, a change of the catalytic behaviour from hydrogenolysis to isomerization has been stated as a consequence of oxygen chemisorption and formation of MO_x species on the carbide surface upon oxygen exposure at room temperature [7].

It has been found that the precursor-derived carbides are attacked by air at room temperature after long exposure times. When h.c.p. Mo_2C synthesized at 900 °C from a peroxide/saccharose precursor is exposed to air for 100 days, only a low increase in mass ($\sim 5\%$) but a dramatic effect on the surface area and porosity is observed. The BET value is reduced by $\sim 50\%$, although the X-ray pattern has been unchanged. It is concluded that atomic oxygen has been substituted for the carbon present in the lattice of the interstitial carbide. WC, however, is by far less affected by oxygen; only a decrease of surface area by $\sim 9\%$ is observed in this period of time.

Simultaneous TGA/differential thermal analysis (DTA) experiments for Mo_2C and WC, both prepared from the peroxide/carbonaceous gels, were carried out to study their high-temperature oxidation under atmospheric pressure. The TGA curves for the non-isothermal oxidation in Fig. 9 demonstrate that the oxidation of Mo_2C begins at a lower temperature (at $\sim$ 180 °C) than that of WC, at $\sim$ 380 °C. The DTA curves reveal some overlapping steps, showing that oxidation proceeds in at least three stages. Although not proved in this study, it is believed that the steps are attributable to the successive processes of formation of oxycarbides, oxidation to oxide species, and burn-off of free carbon. In the lowest temperature region, oxidation may proceed for both carbides by a diffusion process, forming oxycarbides. It is recognized that atomic oxygen can substitute for the carbon present in

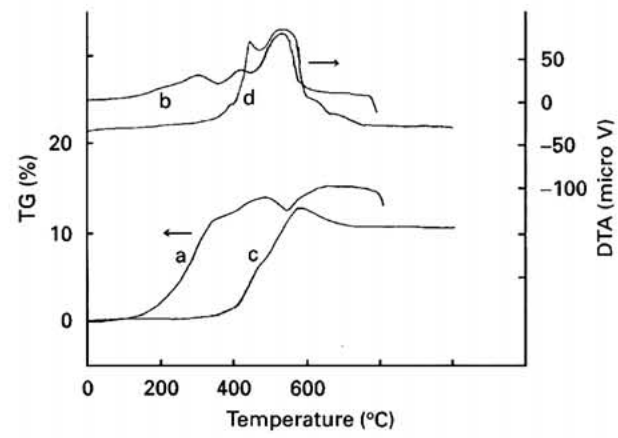

Figure 9 TGA and DTA diagrams of the oxidation of Mo_2C (a and b) and WC (c and d), both produced from the peroxide/carbonaceous gels at 1200 °C.

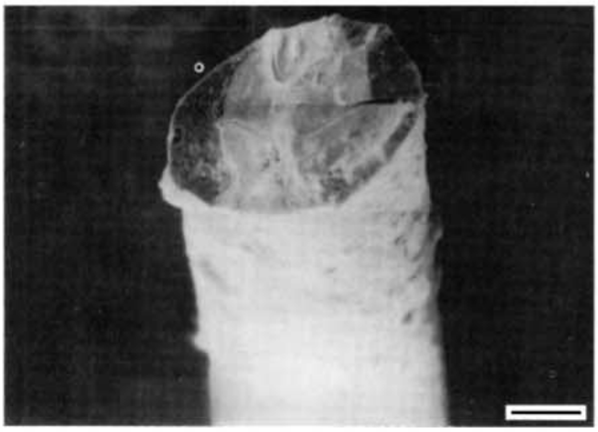

Figure 10 SEM micrograph of a tungsten glycolate/saccharose fibre annealed at 1200 °C (bar length 10 μm).

the carbide lattices. With the progress of oxidation, several MO_x oxides and free carbon are formed. The removal of the carbon as CO_2 is slow because of the difficulty of carbon combustion at low temperatures. Thus, the carbon atoms may be incorporated in the oxide matrices. With the approach to the oxidation end point at ~600 °C, the excess of free and incorporated carbon burns off giving rise to a deeping or descent in the TG curves.

3.6. Formation of fibres and films

In the most typical procedures for fibre formation, fibres are drawn from viscous solutions or sols. The sols containing the peroxo acids or molybdenum and tungsten blue, respectively, became faintly cloudy and increased in viscosity very steeply under heating at 60–70 °C. Thus, attempts to draw fibres from these sols just before they solidified into bulk gels were not successful. Presumably, the viscosity increase with temperature treatment may be due to condensation reactions forming mostly spherical polymers. The sols, however, are suitable for the preparation of films which can be thermally converted into carbide coatings. Gel films are made by dipping a substrate into the sols. After curing at temperatures rising from 50 °C up to 110 °C for approximately 3 h, carbides are formed by heating at 900–1200 °C. Carbide coatings of varying thickness are made by repeated dipping and heating procedures. When a porous alumina foam is used as the substrate, a washcoat of WC on the ceramic foam can be produced. It has been found that this ceramic washcoat serves as an advantageous catalyst support. After doping with rhodium this washcoat catalyst showed a higher catalytic activity for the reforming of CH_4 with CO_2 than a conventional rhodium catalyst with alumina as washcoat on the ceramic foam [33].

Contrary to the sols, the solutions of the ethylene glycolates and saccharose in ethylene glycol show generally better conditions for the occurrence of spinnability. Clearly, the viscosity and spinnability are dependent on the amount of the solvent. Upon concentrating, the solutions exhibit rheological properties that allow for the formation of fibres and films. Hand-drawn fibres were obtained directly by extracting a glass rod from the precursor solutions B, C, E and F at ~50 °C. Fibres of a length of 10–20 cm could be drawn this way. Because the fibres are thermoplastic they were suspended on a glass bar and dried for 1 week at room temperature. The following processing comprised slow heating ($10\,^{\circ}C\,h^{-1}$) up to 150 °C in ambient air, and a high-temperature treatment up to 900–1200 °C at $5\,^{\circ}C\,min^{-1}$ under argon in a graphite boat. Thus, fibres of a silvery brightness composed of WC or Mo(O, C) and excess carbon were obtained. Fig. 10 shows an electron micrograph of a WC/C fibre after annealing at 1200 °C.

The occurrence of spinnability of the ethylene glycolate solutions may be due to condensation reactions of saccharose coupled with fixing of the transition metal glycolates, forming linear polymers. Presumably, the reactions between the glycolates and saccharose may be described in terms of co-ordination bonding between the hydroxy groups of the pyranose and furanose rings of saccharose and the polyvalent cations. The concentration dependence of the viscosity supports the assumption that the polymeric products in the solutions are not spherical but linear.

For film preparation, glycolate/saccharose solutions of lower viscosity than for fibre drawing were used. An alumina foam was immersed in the molybdenum glycolate/saccharose solution C and slowly extracted. After drying first at room temperature for 1 day and then at 150 °C for 1 h, the film was converted at 1000 °C under argon into a mixture of Mo-(O, C) and excess carbon. In order to increase the film thickness, this procedure was repeated leading to a coat of a metallic brightness. Fig. 11 shows a ceramic foam with and without a Mo(O, C) coat. The coating procedure rendered the ceramic foam electrically conductive. An ohmic resistance of 3.9 Ω was measured between two points with a distance of 3.5 cm, showing a nearly metallic conductivity of the coat.

4. Conclusions

The work reported here demonstrates that precursors for the molybdenum and tungsten carbide synthesis can be prepared from aqueous and ethylene glycol

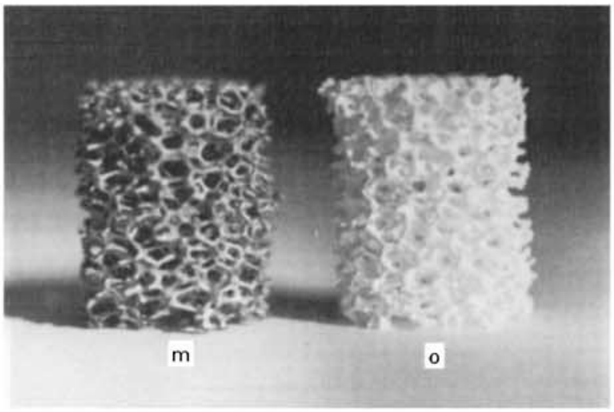

Figure 11 Ceramic foam before (○) and after coating with a C/Mo(O, C) composite (m).

solutions, respectively. The solutions contain a pyrolysable organic compound, such as saccharose or carbonaceous gel, and a soluble molybdenum or tungsten compound which may be a peroxo acid or an ethylene glycolate. The solution route ensures an intimate mixing of the starting compounds, and in some cases, if saccharose is used, a reduction of W^{6+} and Mo^{6+} already in the solution or gel stages. Thus, pyrolysis leads to a homogeneous mixture of the reactants, carbon and suboxides, and consequently to moderate temperatures (800–1200 °C) for the carbothermal reactions. In case of the WC synthesis, a higher reactivity of the saccharose coke in comparison with the carbonaceous gel coke has been found. Advantages of the solution routes are that the costs for the energy intensive carbide syntheses can be reduced. The carbides can be obtained either as fine powders or in shaped forms, as fibres or coatings. Additionally, the solvents used here are not environmentally risky. Finally, the solution routes may offer novel possibilities for the synthesis of ternary carbides, e.g. of M^1M^2C solid solutions. The current work indicates that high surface area carbides can be produced which may be used in catalysis or ceramics.

References

1. P. N. ROSS and P. STONEHART, *J. Catal.* **48** (1977) 42.
2. V. S. PALANKER, D. V. SOKOLSKY, E. A. MAZULEVSKY and E. N. BAYBATYROV, *J. Powder Sources* **1** (1966/1967) 169.
3. M. SAITO and R. B. ANDERSON, *J. Catal.* **63** (1980) 438.
4. L. VOLPE and M. BOUDART, *J. Solid State Chem.* **59** (1985) 332 and 348.
5. J. S. LEE, S. T. OYAMA and M. BOUDART, *J. Catal.* **106** (1987) 125.
6. J. S. LEE, K. H. LEE and J. Y. J. LEE, *J. Phys. Chem.* **96** (1992) 362.
7. E. IGLESIA, F. H. RIBEIRO, M. BOUDART and J. E. BAUMGARTNER, *Catal. Today* **15** (1992) 307.
8. M. J. LEDOUX, S. HAUTZER, C. PHAM-HUU, J. GUILLE and M. P. DESANEAUX, *J. Catal.* **114** (1988) 176.
9. M. J. LEDOUX and C. PHAM-HUU, *Catal. Today* **15** (1992) 263.
10. R. M. LAINE and A. S. HIRSCHON, in "Better ceramics through chemistry II", MCR Symposia, Vol. 73, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (Materials Research Society, Pittsburgh, 1986) p. 373.
11. UBE Industries, Ltd., Japan. Patent 57017 412 (1982).
12. E. LUGSCHEIDER, H. ESCHNAUER, W. GMOEHLING, P. MACKES, H. MEYER-GRUENOW and A. NISCH, Germ. Patent 3 743 357 (1989).
13. H. PREISS, G. OLIEW and K. SZULZEWSKY, *Fuel* **73** (1994) 243.
14. K. SEGAWA, K. OOGA and Y. KEISUSU, *Bull. Chem. Soc. Jpn* **57** (1984) 2721.
15. R. HAUL and G. DUEMBGEN, *Chem.-Ing.-Tech.* **35** (1963) 586.
16. Gmelin Handbook of Inorganic Chemistry, **Mo**, Suppl. Vol. B3b, edited by Ginelin-Institute (Springer-Verlag, 1987) p. 132.
17. C. AUBRY, G. CHOTTARD, N. PLATZER, J.-M. BREGEAULT, R. THOUVENOT, F. CHAUVEAU, C. HUET and H. LEDON, *Inorg. Chem.* **30** (1991) 4409.
18. N. J. CAMPBELL, A. C. DENGEL, C. J. EDWARDS and W. P. GRIFFITH, *J. Chem. Soc. Dalton Trans.* **1989** 1203.
19. T. KUDO, A. ISHIKAWA, H. OKAMOTO, K. MIYAUCHI, F. MURAI, K. MOCHIJI and H. UMEZAKI, *J. Electrochem. Soc.* **134** (1987) 2607.
20. H. PREISS and W. KANT, *Carbon* **32** (1994) 351.
21. F. A. SCHRÖDER and J. SCHERLE, *Z. Naturforsch.* **28b** (1973) 46.
22. S. AYYAPPAN and C. N. R. RAO, *Mater. Res. Bull.* **30** (1995) 947.
23. J. BOOTH, T. EKSTRÖM, E. IGUCHI and R. J. D. TILLEY, *J. Solid State Chem.* **41** (1982) 293.
24. O. GLEMSER, J. WEIDELT and F. FREUND, *Z. Anorg. Allg. Chem.* **332** (1964) 299.
25. R. PICKERING and R. J. D. TILLEY, *J. Solid State Chem.* **16** (1976) 247.
26. L. E. TOTH, "Refractory materials: transition metal carbides and nitrides" (Academic Press, New York, 1971).
27. E. K. STORMS, "Refractory materials: The refractory carbides" (Academic Press, New York, 1967).
28. J. P. HARE, W. K. HSU, H. W. KROTO, A. LAPPAS, K. PRASSIDES, M. TERRONES and D. R. M. WALTON, *Chem. Mater.* **8** (1996) 6.
29. I. F. FERGUSON, J. B. AINSCOUGH, D. MORSE and A. W. MILLER, *Nature (London)* **202** (1964) 1327.
30. L. LECLERCQ, K. IMURA, S. YISHIDA, T. BARBEE and M. BOUDART, in "Preparation of Catalysts II", edited by B. Delmon, P. Grange, P. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1979) p. 627.
31. H. PREISS, L. M. BERGER and K. SZULZEWSKY, *Carbon* **34** (1996) 109.
32. H. PREISS, D. SCHULTZE and P. KLOBES, *J. Eur. Ceram. Soc.* submitted.
33. G. LIETZ, H. BERNDT, H. PREISS, R. TAMME and J. VÖLTER, in Preprints of the Catalysis Conference CATSA, Rustenburg, South Africa, June 1995, p. 9.

Received 19 August 1996
and accepted 12 September 1997