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Preparation of NbC, TaC and Mo_2C fibres and films from polymeric precursors

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Polymeric precursors for carbothermal reactions were prepared from niobium alkoxide, tantalum alkoxide and molybdenum ethylene glycolate, respectively, by simultaneous reaction with a chelating reagent (acetylacetone) and organic compounds having two or more reactive OH groups, such as ethylene glycol, saccharose, tartaric acid or dihydroxybenzenes. The precursors exist in common polar and non-polar solvents mostly as linear polymers. The viscous solutions show rheological properties that allow for the preparation of polymer fibres and films. At temperatures up to 1500 °C, bulk precursors as well as fibres and films were thermally converted into carbide powders, fibres and coatings. The structural transformations of the polymeric materials into carbides were investigated using simultaneous thermogravimetric–differential thermal analyses (TGA–DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). © *1998 Kluwer Academic Publishers*

1. Introduction

Carbide-based non-oxide ceramics with shaped forms, such as fibres and films, are ideal high-temperature materials because of their high mechanical and thermal stability. The technological importance of SiC fibres, for instance, is based on their application as reinforcing components. Transition metal carbides are also interesting because of their electric and catalytic properties. The current techniques for their fabrication as shaped forms, however, are mostly limited to the formation of chemically or physically deposited films. There has been little attempt at the production of transition metal carbide fibres since appropriate precursors cannot be obtained easily.

Recently, TiC fibres have been produced from polymeric titanate obtained from the ester exchange reaction of titanium alkoxide and diacetates as precursor [1]. TiC, ZrC and WC fibres have also been prepared by fixing the metal cations to cellulose acetate [2], phenolic resin [3] or saccharose-derived polymers [4]. These approaches eliminate the synthesis of polymeric metalates as precursors. Unfortunately, the polymers are mostly insoluble in common solvents and the final products contain a high portion of free carbon.

In this communication the preparation of polymeric metalate precursors, which meet requirements for the production of films as well as fibres, is described. In order to fabricate dense inorganic fibres, it is necessary that

1. The precursor exhibits a homogeneous reactant distribution and a controlled stoichiometry.
2. The precursor or the precursor solution has a high viscosity to facilitate fibre formation.
3. The precursor contains one-dimensional long-shaped polymers.

The first criterion, which is the primary reason for starting with a solution, enables the formation of a uniform fine-grained microstructure. Since the precursor may be thermoplastic, deformation is a problem inherent with fibre drawing. In general, this deformation should be less the lower the quantity of solvents and decomposition products evolved during the thermal processes. The third criterion does not mean that the nature of the polymers is limited only to single-chain polymers, but multiple-chain polymers may also be spinnable. It should be stressed, however, that three-dimensional polymerization leads to heavy cross-linking and to non-spinnability.

With these requirements in mind, NbC, TaC and Mo_2C precursors are developed, which are preferably comprised of linearly connected polymers. The principle of precursor design is based on the simultaneous use of chelating and bridging ligands reacting with transition metal alkoxides. Strong bidentate chelating ligands, such as β-diketones, are suitable for satisfying the maximum co-ordination number of the transition metal ions (six–eight) and for controlling nucleophilic substitution reactions. Thus, linear polymerization instead of three-dimensional condensation may occur if precursor synthesis are accomplished starting not from the alkoxides but from their chelate derivatives. Synthesis routes by simultaneous use of chelating and bridging

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ligands have been proved favourable for the preparation of spinnable TiC and ZrC precursors [5].

The existence of chelate derivatives of niobium and tantalum alkoxides is reported in the literature [6]. $L_nM(OR)_{5-n}$ (where L is an acetylacetonato group) derivatives with varying number of n have been synthesized from $Nb(OR)_5$ or $Ta(OR)_5$ and acetylacetone; reaction at room temperature leads to products with $n = 1$, higher n is achieved under heating. These complex derivatives result as red-brown, highly viscous liquids composed of monomers with a co-ordination number of six. Using ethyl acetoacetate as the chelating ligand, a yellow analogue can be obtained [7, 8]. The presence of chelating ligands in these derivatives enables a slow-down of their reactivity and control of the exchange of the OR groups. For the sixth group transition metals no such alkoxy derivatives but complexing compounds of molybdenum with acetylacetone (acacH), in which Mo can be five- to eight-fold coordination, e.g. $MoO_2(acac)_2$, are hither-to known [9].

The object of this paper is to study the ligand exchange of OR groups in the $L_nM(OR)_m$ derivatives by organic reactants having two or more reactive OH groups, and to prepare linearly polymeric precursors by condensation polymerization. The precursors are investigated based upon their solubility, ability to form films and fibres (spinnability), and thermal behaviour. Synthesis and carbothermal conversion of the polymeric precursors into carbides are described below.

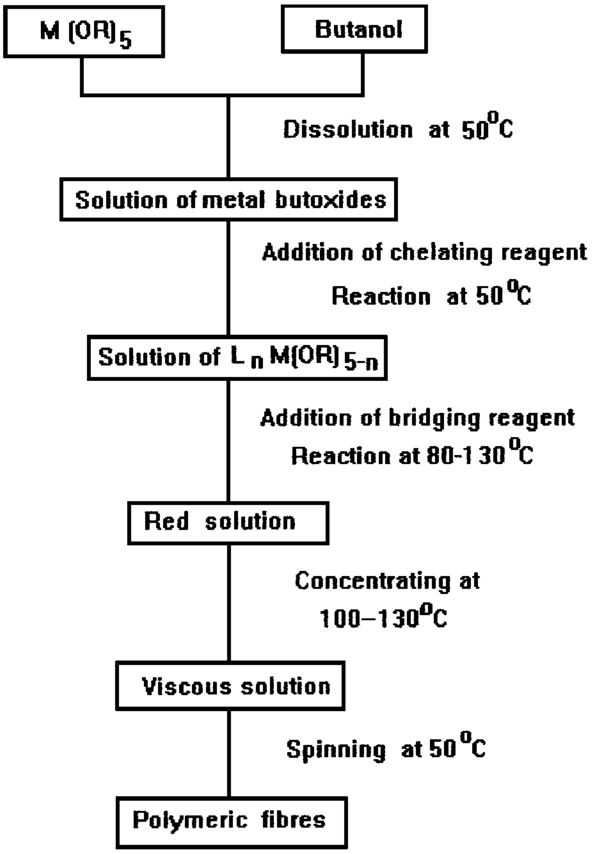


Figure 1 Scheme of the experimental procedure used for the fabrication of niobium and tantalum polymer fibres.

2. Experimental procedure

2.1. Synthesis of niobium and tantalum precursors

A scheme of the experimental procedure for niobium and tantalum precursors is illustrated in Fig. 1.

Some 2.5 g of reagent grade acetylacetone (25 mmol) were added to a solution of 3.18 g $Nb(OC_2H_5)_5$ (10 mmol) (Aldrich Chemie AG) in 5 ml n-butanol and heated under nitrogen at 50 °C for 1 h. The colour of the solution changed upon heating to yellow, showing that alkoxide derivatives of type $(acac)_n\ Nb(OR)_{5-n}$ had formed. Now the hydrolysability of the starting alkoxides is reduced, and further operations can be performed in open atmosphere. After the temperature of the solutions had been increased to 80 °C, the materials that serve as bridging ligands were added. The appropriate amounts of these bridging materials are listed in Table I (the amounts are chosen to adjust the carbon content necessary for carbide formation). In the case of saccharose and tartaric acid, dissolution took about 1 h. Then the solutions were heated under reflux at the reaction temperatures given in Table I, whereby the colour changed in characteristic ways: with saccharose, catechol and hydroquinol to red, with tartaric acid to light brown, and with resorcinol to green. Concentrating the solutions at the same reaction temperatures led either to spinnable solutions or to elastic gels (see Table I).

Some 2.5 g acetylacetone (25 mmol) were added to a solution of 4.06 g $Ta(OC_2H_5)_5$ (10 mmol) (Fluka AG) in 5 ml n-butanol, and the mixture was heated under nitrogen at 50 °C for 1 h. The colour of the solution changed to pale yellow, showing that alkoxide derivatives of type $(acac)_n\ Ta(OR)_{5-n}$ had formed. Now, further operations were performed in open air. After the temperature of the solutions had been increased to 80 °C, materials which serve as bridging ligands were added and heating was continued until dissolution was observed (the amounts of the bridging materials match those given in Table I). Then the solutions were heated under reflux at the reaction temperatures given in Table I, whereby the colour of the solutions changed in a characteristic way: with ethylene glycol, tartaric acid and hydroquinol to intensive yellow, and with saccharose, catechol and resorcinol to red-brown. Evaporation of the solvents, mostly butanol, at the same reaction temperature led first to elastic gels or concentrated viscous solutions, and lastly to neat precursors. The precursors were tested for solubility, spinnability, and thermal behavior.

2.2. Synthesis of molybdenum carbide precursors

Some 1.69 g molybdic acid (Merck AG), which has an assay of 10 mmol MoO_3, were dissolved in 5 ml ethylene glycol and glycerol, respectively, under heating at 80 °C. Heating was carried on until the odour of ammonia could no longer be detected (commercial molybdic acid contains ammonium molybdate). Then the temperature was increased upto 110 °C, whereby the colour of the solution changed to green and lastly to brown, and the solvent was allowed to evaporate partially. The

TABLE I Properties of acetylacetonato metalate precursors with various bridging ligands

Polymer type[a]	Quantity of bridging ligand/10 mmol metal (g)	Reaction temperature (°C)	State of concentrated polymer solution	Spinning solvent[b]	Carbon total of final product (wt %)
NbEg	0.62	80	Elastic gel		9.7
NbSa	0.65	130	Spinnable	Bu, Pr	11.9
NbTt	2.40	130	Spinnable	Bu, Pr	10.5
NbCa	0.50	100	Spinnable	Bu, Pr, Be, To	12.9
NbHy	0.49	80	Elastic gel		12.5
NbRe	0.40	100	Spinnable	Bu, Be	13.3
TaEg	0.62	110	Spinnable	Bu	5.2
TaSa	0.66	130	Spinnable	Bu, Pr, Be, To	6.0
TaTt	2.40	130	Spinnable	Bu, Pr, Be, To	5.3
TaCa	0.48	100	Spinnable	Bu, Pr, Be, To	7.1
TaHy	0.49	80	Elastic gel		6.5
TaRe	0.40	100	Spinnable	Pr	6.7
MoEg$_1^c$	5.0	110	Spinnable	Ethylene glycol	5.3
MoEg$_2^d$	5.0	110	Spinnable	Ethylene glycol	8.8
MoGl[d]	5.0	110	Spinnable	Glycerol	9.0

[a] Bridging ligand: Eg, ethylene glycol; Gl, glycerol; Sa, saccharose; Tt, tartaric acid; Ca, catechol; Hy, hydroquinol; Re, resorcinol.

[b] Bu, n-butanol; Pr, n-propanol; Be, benzene; To, toluene.

[c] Molar ratio acetylacetone: metal = 1.

[d] Molar ratio acetylacetone: metal = 2.

brown colour is indicative of the reduction of Mo^{+6} to Mo^{+4}. The concentrated solutions were allowed to cool to approximately 90 °C, and different amounts of acetylacetone (10 or 20 mmol) were added. These mixed solutions were suitable for the production of polymer films. Otherwise, heating was continued at 90 °C until the concentrated solutions showed the occurrence of spinnability. Best spinnability was observed at approximately 50 °C; at room temperature a glass-like residue was formed. Exposure to air for a long time rendered the solutions as well as the glass-like material green and lastly blue. This change of colour is indicative of reoxidation of Mo^{+4} by oxygen from the air.

2.3. Heat treatment

The bulk precursors as well as the fibres and coated substrates were annealed in alumina boats using an alumina tube furance (Carbolite Furnace Limited) at 500–1500 °C with 50 or 100 °C intervals in flowing argon. The heating rate was adjusted to 5 °C min^{-1} and the holding time at maximum temperature to 1 h.

2.4. Characterization methods

The thermal behaviour of the bulk precursors in argon was studied by simultaneous thermogravimetry–differential thermoanalysis (TGA–DTA) upto 1600 °C. The heating rate was 10 °C min^{-1}. Conventional X-ray diffractometry (XRD) with filtered CuK_α radiation was used to record the X-ray diffractograms.

Carbon analysis of the heat-treated bulk precursors was performed with a CHN-Analyser EA 1110 (CE Instruments). The microstructure of the surface and cross-section of the carbide fibres was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Precursor preparation

Organogels are formed spontaneously when niobium and tantalum alkoxides react with polyols, such as ethylene glycol or glycerol. The behaviour of these alkoxides resembles that of the alkoxides of the fourth group of the periodic table. Recently, gelling of $Zr(OR)_4$ with ethylene glycol has been studied, and three-dimensional condensation by bonding via glycolate bridges of the type $-Zr-O-CH_2-CH_2-O-Zr-$ have been stated [10]. The behaviour of transition metals of the sixth group, however, is different. The ethylene glycolates of Mo and W of valency four, five or six are soluble in ethylene glycol [4].

Here, it has been found that condensation of niobium and tantalum alkoxides with ethylene glycol is reduced when acetylacetone is present. A molar ratio of acacH : Ta of 2–3 is suitable for the preparation of a stable solution (sol); for niobium the solution becomes slightly elastic in nature at the same molar ratio. This slow-down of reactivity is due to the complexing ability of the acac ligands (expansion of the co-ordination number) in the monomeric alkoxide derivatives $(acac)_nM(OR)_{5-n}$ formed in the solutions. It has to be noted that these derivatives are remarkably stable against hydrolysis. This may be due to the moisture stability lent to the alkoxides by the incorporated ligands. For the molybdenum glycolates, the formation of complex compounds is also suggested because compounds of molybdenum with acac groups, in which Mo^{+4}, Mo^{+5} or Mo^{+6} can be five-to-eight-fold co-ordinated, are known [9]. Experiments with ethyl acetoacetate instead of acetylacetone were not successful in obtaining stable clear precursor solutions, so this kind of chelating ligand was given up for further experiments.

In order to produce polymeric precursors, $(acac)_n M(OR)_{5-n}$ derivatives were reacted with organic compounds having two or more reactive OH groups to act as bridging ligands, such as ethylene glycol, saccharose, dihydroxycarboxylic acids and dihydroxybenzenes. Because of their chemical functionality carboxylic acids may behave both as chelating and as bridging ligands [11]. For producing polymeric molybdenum precursors, the solvent ethylene glycol simultaneously serves as a bridging ligand.

Transesterification of the OR groups in the $(\mathrm{acac})_n\mathrm{M(OR)}_{5-n}$ derivatives and condensation polymerization are the reactions that occur in the solutions upon heating. The overall equation for the formation of polymeric precursors can be written for case $n = 3$

$$\begin{aligned} m(\mathrm{acac})_3\mathrm{M(OR)}_2 + m\mathrm{HO{-}X{-}OH} &\rightarrow \\ -[-\mathrm{O{-}(acac)_3M{-}O{-}X}-]_{m}- + m\mathrm{ROH} & \quad (1) \end{aligned}$$

In parallel, self-condensation of the derivatives is also possible according to

$$\begin{aligned} m\,(\mathrm{acac})_3\mathrm{M(OR)}_2 \rightarrow -[-(\mathrm{acac})_3\mathrm{M{-}O}-]_{m}- \\ + m\mathrm{R{-}O{-}R} \quad (2) \end{aligned}$$

This self-condensation then leads to metaloxane polymers with M–O–M bridges. It is assumed that the polymeric precursors here formed contain both M–O–X–O–M and M–O–M bridges in the polymer chains. Moreover, double- and multiple-chain polymers with mainly M–O–M interconnecting bonds will occur, too.

During the transesterification of the OR groups a change of colour of the reaction solutions is observed. Dissolution of saccharose takes 1–2 h and renders the solution deep red. Transesterification and polymerization in the solutions, however, are incomplete, especially when dihydroxybenzenes are used, although sometimes spinnable solutions are formed upon these preparation conditions. If one refers to general slow esterification kinetics with phenols, the incompleteness of the reactions is understandable. In order to force the reactions to completion, higher reaction temperatures than allowed in the solution are needed. Polymerization condensation, which requires the full elimination of alcohol and ether produced according to Equations 1 and 2, will occur at higher temperatures (150–350 °C). This has already been stated for the analogous titanium and zirconium precursors [5]. The systems are complicated, as precursor degradation will occur simultaneously (see Section 3.3).

There is another point of complication. Self-condensation according to Equation 2 and even condensation polymerization (Equation 1), especially when the bridging unit X stems from ethylene glycol, can lead not only to multiple-chain polymers but also to three-dimensionally connected networks. Thus, the process of concentrating gives the solutions an elastic nature without any spinnability of these elastic gels. In order to avoid three-dimensional condensation the ligand–metal ratio was varied in preliminary experiments. The best conditions that match spinnability as well as carbon contents necessary for carbidation were found for an acacH : metal ratio of 2.5 and the amounts for the bridging ligands given in Table I. However, Table I shows that spinnability did not occur in all cases.

3.2. Spinnability and film production

Since fibre drawing from solutions is the most typical procedure for fibre production, precursors as-received at the reaction temperature (see Table I) and dried for 1 h at this temperature were tested for solubility in various common solvents. It has been proved that most of the niobium and tantalum precursors are soluble in polar solvents, such as n-butanol and n-propanol, as well as in non-polar solvents, such as benzene and toluene. The molybdenum precursors, however, are soluble only in ethylene glycol and glycerol. Upon concentrating the solutions they exhibit rheological properties that allow for fibre formation. The viscosity of the solutions increases with concentration. This concentration dependence supports the assumption that the precursors exist preferentially as linear polymers.

Fibres were hand-drawn by extracting a glass rod from the viscous solutions at 40–50 °C. Sometimes the solutions, which resulted as elastic gels with precursor synthesis, also showed the occurrence of spinnability before they gelled. This behaviour was found for the NbHy and TaHy precursors, but only short fibres could be drawn. Spinnability was estimated by the length of the drawn fibres (spinnability in Table I means that fibres of a length of >20 cm could be drawn). Since the fibres were more or less thermoplastic and could therefore deform upon drying, they were suspended on a glass bar and dried at room temperature for one week before they were dried and pyrolysed. Fig. 2 gives an example of the appearance of the TaRe polymer fibre after drying.

The occurrence of spinnability can also be applied to the fabrication of polymer films and, finally, carbide coatings. For film preparation, precursor solutions of a lower viscosity than for fibre drawing were used. Either alumina foams or rods were immersed in a precursor solution (of approximately 20 wt %) NbTt and TaSa, respectively, in butanol, or $\mathrm{MoEg_2}$ in ethylene glycol, and slowly extracted. After exposure to air at room temperature for one week the films were heated to 150 °C and dried for 1 h. Then the NbTt and TaSa films were pyrolysed under argon up to 1500 °C, and that of $\mathrm{MoEg_2}$ up to 1200 °C.

3.3. Decomposition of niobium and tantalum precursors

XRD and simultaneous TGA–DTA have demonstrated similar thermal behaviour for the different niobium and tantalum bulk precursors. Some XRD results are summarized in Table II. The TGA, differential thermogravimetric analysis (DTGA) and DTA curves of NbRe and TaRe obtained under argon at 20–1600 °C are given in Figs 3 and 4 as typical representatives. The data show two temperature ranges of strong mass loss: the first one includes the decomposition processes occurring up to approximatley 550 °C, and the second one is that of carbothermal reduction above approximatley

TABLE II Phases determined by XRD during the thermal treatment of Nb, Ta and Mo precursors

Temperature °C	Nb	Ta	Mo
800	Nanocrystal $Nb_2O_5^*$	Nanocrystal $Ta_2O_5^*$	
900	Orthorhombic Nb_2O_5	Orthorhombic Ta_2O_5	$Mo + Mo_2C$
950	Tetragonal NbO_2	Orthorhombic Ta_2O_5	$Mo + Mo_2C$
1000	NbO_2 + (NbC)	Ta_2O_5 + (TaC)	$Mo + Mo_2C$
1100	NbO_2 + NbC	Ta_2O_5 + TaC	$Mo + Mo_2C$
1200	NbO_2 + NbC	Ta_2O_5 + TaC	Mo_2C
1300	NbC	Ta_2O_5 + TaC	
1400	NbC	TaC	

*X-ray amorphous.

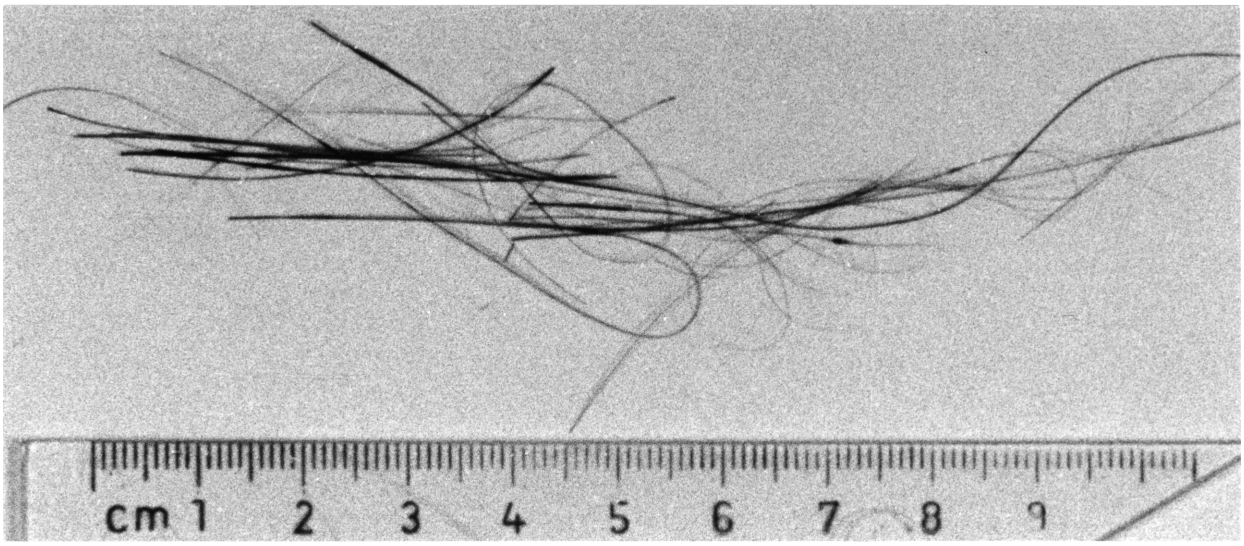


Figure 2 Macroscopic appearance of TaRe polymer fibres as-synthe-sized.

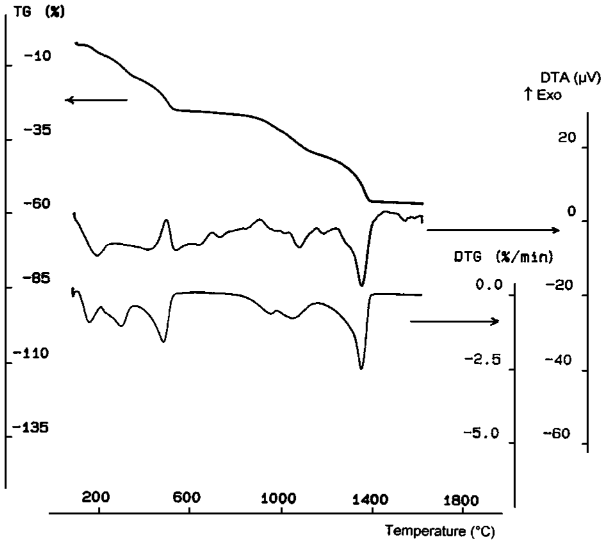


Figure 3 TGA, DTGA and DTA curves of NbRe precursor obtained under argon.

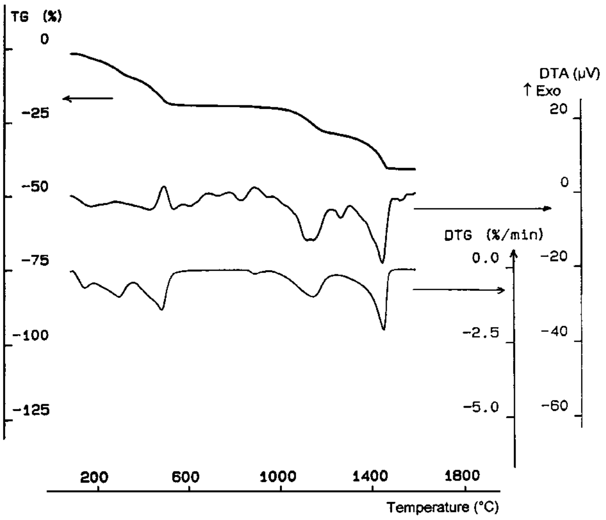


Figure 4 TGA, DTGA and DTA curves of TaRe precursor obtained under argon.

900 °C. The intermediate section at 550–900 °C is characterized by a very low mass loss of only about 2%.

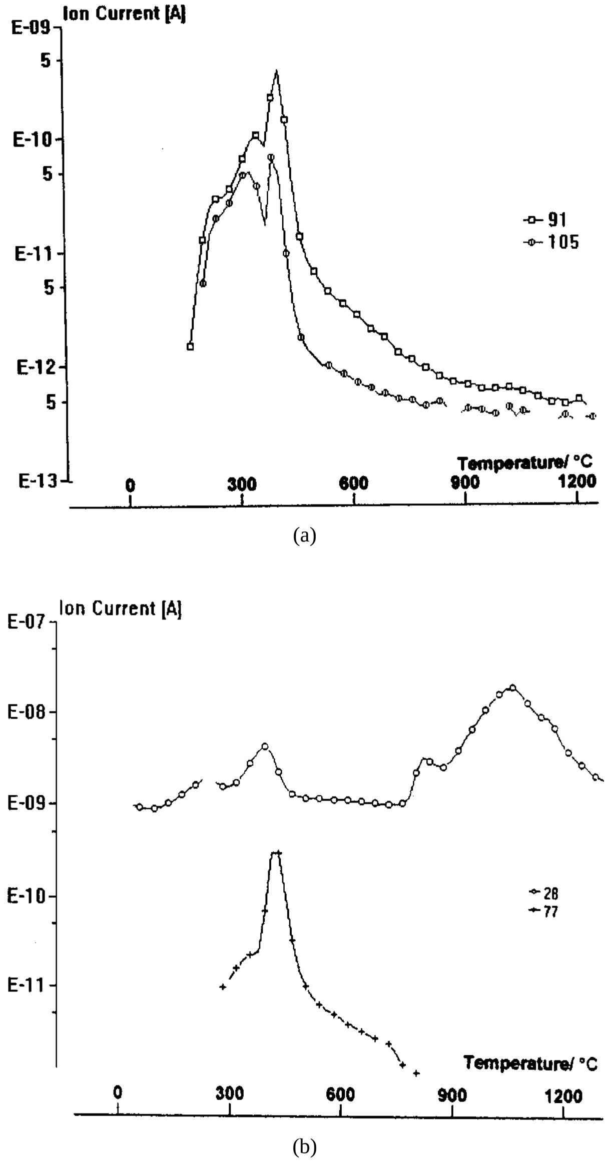
The DTGA and DTA curves indicate that both precursors undergo multi-step reactions during their decomposition. The first mass loss peak immediately after the beginning of heating, which coincides with an endothermic DTA peak, is attributable to the evaporation of solvents entrapped in the precursors assynthesized. The following DTGA mass loss peak is broader than the first one and reaches up to 350 °C. It is assumed that this mass loss is due to completion of the condensation reaction according to Equations 1 and 2. For analogous titanium and zirconium precursors this assumption has been confirmed by Fourier transform infrared (FTIR) spectral investigations; the infra-red (I.R.) spectra revealed the elimination of alkoxide groups attached to Ti and Zr up to 350 °C [5].

The third decomposition mass loss from approximately 350 to approximately 550 °C is seemingly correspondent with a broad endothermal signal superimposed by a striking exothermic peak centred at approximately 500 °C. These thermal events are interpreted as the result of degradation of the acetylacetone and resorcinol groups attached to Nb and Ta, respectively. Unlike the decomposition of the alkoxide groups, the decomposition of these groups results in the formation of carbon as a coke. Coking reactions are always endothermic as widely known. The complexity of the ligands entails a broad endothermic signal. The superimposed exothermal peak may be assigned to structural changes that involve destruction of M–O–C bondings, releasing residual organic groups, and the formation of M–O–M bondings. These structural transformations result in octahedral MO_6 units, however, with a high degree of disordering or short-range ordering as commonly found with amorphous or nanophase oxides. Such oxides without the long-range order of crystalline Nb_2O_5 or Ta_2O_5 are supposed to be formed at approximately 500 °C and are homogeneously dispersed within an amorphous carbon network. XRD did not show the presence of any crystalline phases at 600–700 °C. By simultaneous mass spectrometric investigations it could be demonstrated that aromatic groups attached to the metal atoms are those that are released in this last decomposition step. Monitoring of the decomposition products in the vapour phase shows maxima of the tropylium cation ($C_7H_7^+$, m/e = 91) and benzoyl cation ($C_7H_5O^+$, m/e = 105) in this decomposition range of the TaRe precursor (Fig. 5a). Both the maxima as well as the maxima of the fragmentation products of the benzoyl cation ($C_6H_5^+$, m/e = 77; and CO^+, m/e = 28) correspond very well with the superimposed exothermic DTA peak (Fig. 5b). The second CO^+ peak at approximately 900 °C refers to the onset of carbothermal reduction.

According to the XRD results, Nb_2O_5 and Ta_2O_5 begin to crystallize in their orthorhombic forms between 800 and 900 °C. The diffraction lines at 850 °C are broad, indicating the presence of crystallites of nanometre size, as was also found for gel-derived precursors [12]. The exothermic peaks in the DTA diagrams at 850–900 °C (Figs 3 and 4) can be assigned to these crystallization processes. Compared with single oxide gels and gel-derived carbide precursors [12], the crystallization temperatures of the oxides in the precursors investigated here are higher, showing that the coke matrix produced from the polymeric precursors heavily opposes the processes of nucleation and crystal growth.

3.4. Carbothermal reduction of the bulk precursors

The TGA curves in Figs 3 and 4 show that carbothermal reduction reactions in niobium and tantalum precursors start immediately after the crystallization processes, at approximately 900 and 1000 °C. This low onset temperature of carbothermal reduction compared with conventional oxide–carbon blends is explained by the intimate mixing of reactants in the precursors.



(a)

(b)

Figure 5 Mass spectroscopic monitoring of representative fragmentation ions during decomposition of the TaRe precursor: m/e = 105 and 91 (a); and m/e = 77 and 28 (b).

The DTGA curves reveal a three-step mechanism for the Nb precursor (Fig. 3) and a two-step mechanism for the Ta precursor (Fig. 4). According to XRD results, the first DTGA minimum at approximately 950 °C for NbRe is caused by the formation of NbO_2 (Table II). It is plausible that such a DTGA minimum is not observable for the Ta precursors because no tantalum suboxides are known. Both DTGA peaks during the reduction of Ta_2O_5 are attributable to TaC formation. XRD patterns of precursors annealed in the carbolite furnace show the simultaneous presence of Ta_2O_5 and TaC at 1100–1300 °C and only TaC above 1300 °C (a shift to somewhat lower temperatures in the XRD patterns compared to the DTGA curves is explained with the longer holding time at maximum temperature for the oven experiments). A similar reduction behaviour, but with simultaneous occurrence of NbO_2 and NbC, was concluded from XRD for the Nb precursors between 1000 and 1200 °C. Therefore not the formation of any intermediary products, but kinetic effects ought to be responsible for splitting of the reduction processes.

Pores caused during the first carbidation step cause an interruption of the intimate contact of oxides and carbon. On the other hand, oxide particles are allowed to grow. Both effects slow down the reaction rates of reduction of the oxides—either by carbon or CO— and higher temperatures are required to increase carbon diffusion and to complete the carbidation. XRD confirms that the final products are already NbC at 1400 °C and TaC at 1500 °C; the patterns in Fig. 6 are nearly identical with those given in the JCPDS cards 38-1364 (NbC) and 35-801 (TaC).

TGA indicated thermal behaviour of molybdenum precursors, which is diferent from that of Nb and Ta precursors. The TGA and DTGA curves of $MoEg_1$ in Fig. 7 show that mass loss, already observed upon the start of heating, continues up to the end point of carbothermal reduction and does not run through a horizontal section of constant mass. Therefore, it is concluded that precursor decomposition and reduction reactions are interlocked. Shortly before reaching its end point at approximately 850 °C mass loss considerably accelerates. At this end point the presence of Mo metal and hexagonal Mo_2C (JCPDS card 35-787) was proved by XRD for $MoEg_1$ as well as for the $MoEg_2$ precursor, showing that reduction is finshed; however, carburization of the Mo metal is incomplete. In order to force carburization to completion, an increase in temperature up to 1200 °C was necessary. After 1200 °C heating for 1 h, the XRD pattern of $MoEg_1$ revealed predominantly Mo_2C beside somewhat Mo metal, but only the lines of M_2C were found for $MoEg_2$. The diagram of $MoEg_2$ is shown in Fig. 6. XRD results are consistent with the carbon analyses: $MoEg_1$ produces upon pyrolysis less carbon and $MoEg_2$ more carbon than necessary for the formation of Mo_2C.

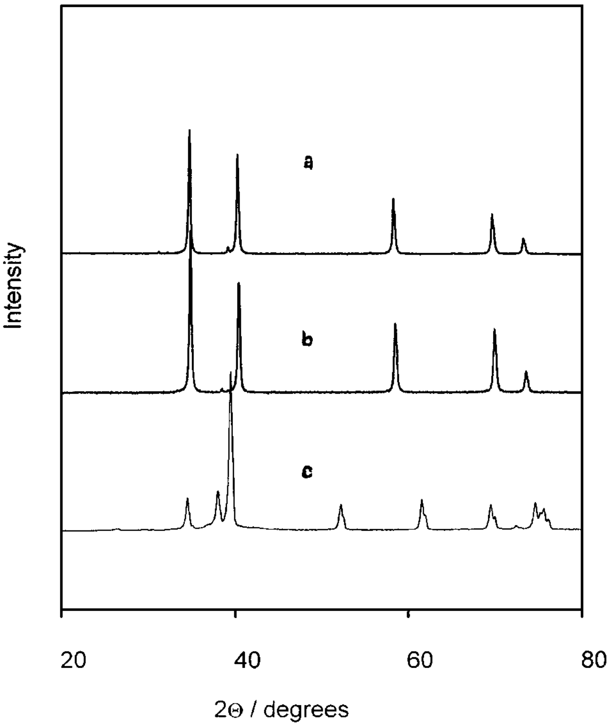


Figure 6 XRD patterns of NbSa precursor (a), TaSa precursor (b) annealed at 1400 °C, and $MoEg_2$ precursor annealed at 1200 °C (c).

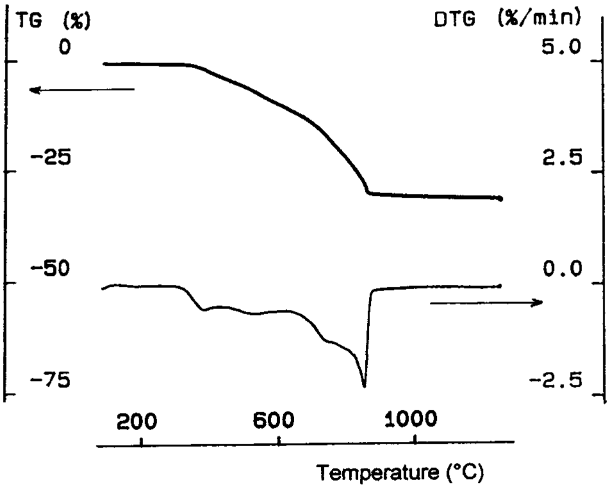


Figure 7 TGA and DTGA curves of $MoEg_1$ precursor obtained under argon.

3.5. Carbothermal conversion of polymer fibres and films into carbide fibres and films

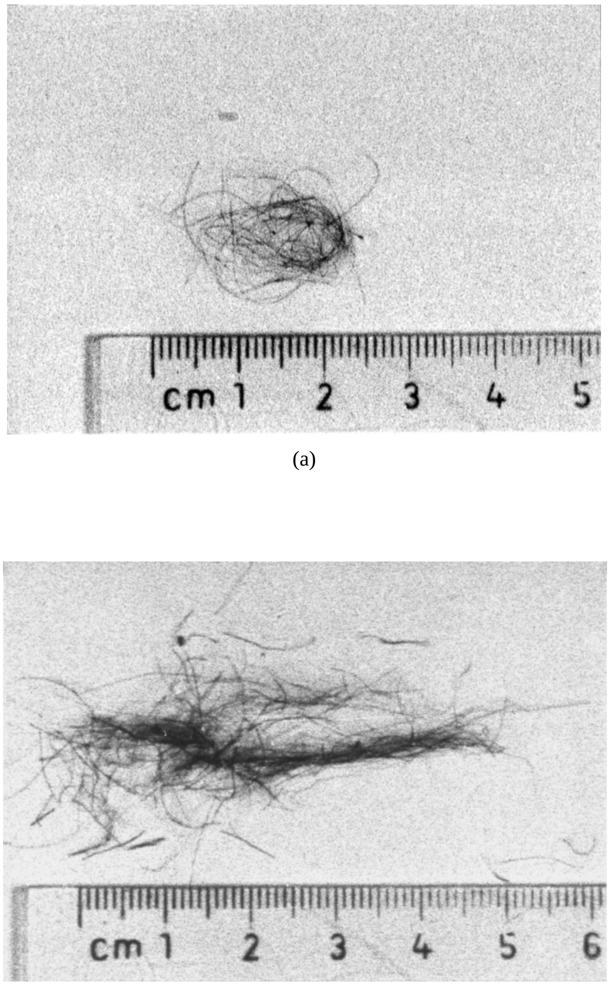
Since deformation of the thermoplastic polymer fibres and the expulsion of solvents and reaction products are the most detrimental effects that influence stability and shrinkage, the fibres were carefully processed during drying and heating. We have found that long-time exposure to air (for approximately one week) and slow heating (10 $^{\circ}Ch^{-1}$) prevents deformation of the fibres during drying. The colour of the molybdenum polymer fibres changed in air to blue, showing that oxidation of Mo^{+4} to a valency state of Mo^{+5}/Mo^{+6} had occurred. Presumably, this reoxidation stabilizes the fibre form, too.

During heat treatment of the niobium and tantalum polymer fibres decomposition reactions and carbothermal reduction produce a lot of byproducts. Therefore, a heating rate of 5 °C min^{-1} was chosen for pyrolysis of fibres and films up to 1500 °C. Nevertheless, stable carbide fibres could not be obtained in all cases; the fibres produced using ethylene glycol were the most brittle ones. It is thought that much lower heating rates will be more successful.

For producing molybdenum carbide fibres it has been proven that fibre stability is less sensitive to heating rate. The best molybdenum carbide fibres were obtained by heating the polymer fibres at a rate of 8 °C min^{-1} up to 1200 °C and holding the maximum temperature for 1 h. Fig. 8a shows the macroscopic appearance of NbC fibres and Fig. 8b that of Mo_2C fibres.

3.6. Characterization of carbide fibres and films

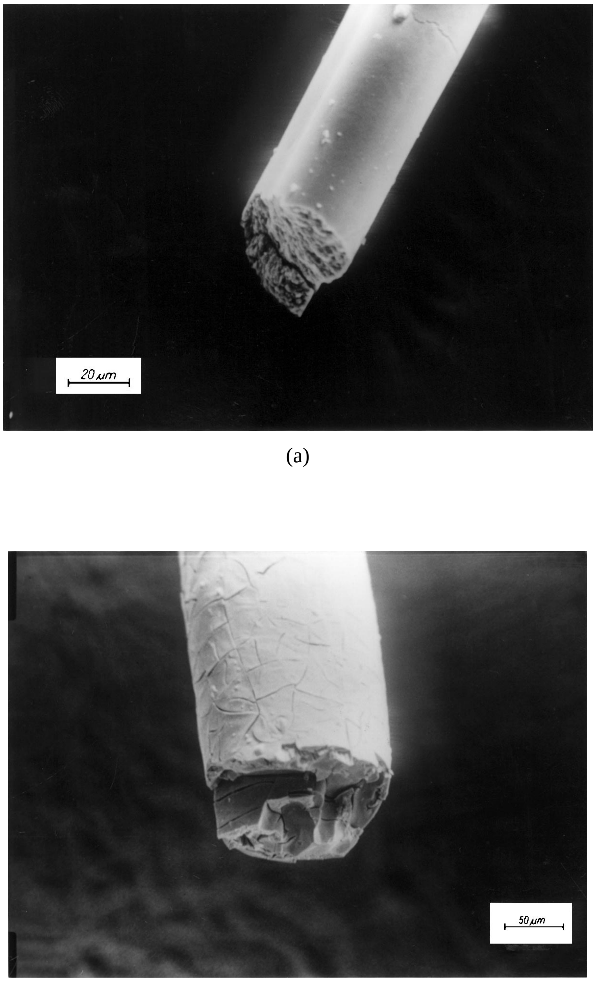
The final fibres and films are composed of crystalline phases of NbC, TaC or Mo_2C with or without additional free carbon. The amount of free carbon was determined either from the quantities of the oxides Nb_2O_5, Ta_2O_5 or MoO_3 resulting from oxidation experiments



(a)

(b)

Figure 8 Macroscopic appearance of carbide fibres obtained from NbRe precursor at 1400 °C (a), and $MoEg_1$ precursor at 1200 °C (b).



(a)

(b)

Figure 9 Electron micrographs of carbide fibres obtained from NbSa (a), and TaSa (b), precursor.

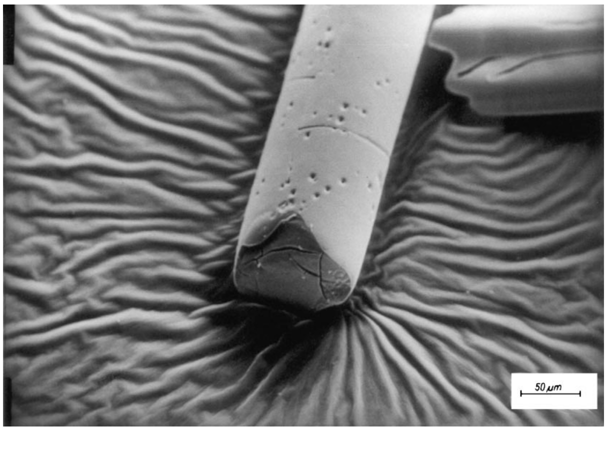


Figure 10 Electron micrographs of carbide fibres obtained from $MoEg_1$ precursor.

(see later) or from chemical analyses of the total carbon content of precursor samples, which were heat treated along with the fibres. The determined concentration of total carbon is summarized in Table I and shows a content of free carbon of 0–3 wt % in comparison with the theoretical values of bonded carbon (11.44 wt % for NbC; 6.22 wt % for TaC; 5.89 wt % for Mo_2C).

The quality of the carbide fibres was investigated using scanning electron microscopy (SEM). Fig. 9 shows carbide fibres obtained from NbSa and TaSa precursors at 1400 °C. The fibre diameters range between 30 and 100 μm. The NbC fibre shows that the carbothermal treatment yields, in this case, fibres with a smooth surface, and consisting of sintered sub-micrometre-sized grains. The TaC fibre (Fig. 9b) shows more cracks; however, no pores are observed in the fracture surface. The fibre is very fragile to handle. The micrograph in Fig. 10 shows surface features of a typical Mo_2C fibre. The surface is slightly porous and the cross-section is mainly smooth. Presumably, the pores may be due to solvents and reaction products evolved during the heating processes.

Fig. 11 shows an alumina foam with a tantalum carbide coating and an alumina rod coated with molybdenum carbide. The coating procedures rendered the ceramic materials electrically conductive. Measurements of ohmic resistances showed nearly metallic conductivity of the foam and the rod.

The stability of the carbide materials versus oxidation were investigated by TGA measurements in flowing air. The oxidation experiments were performed with bulk precursors first heated under argon up to

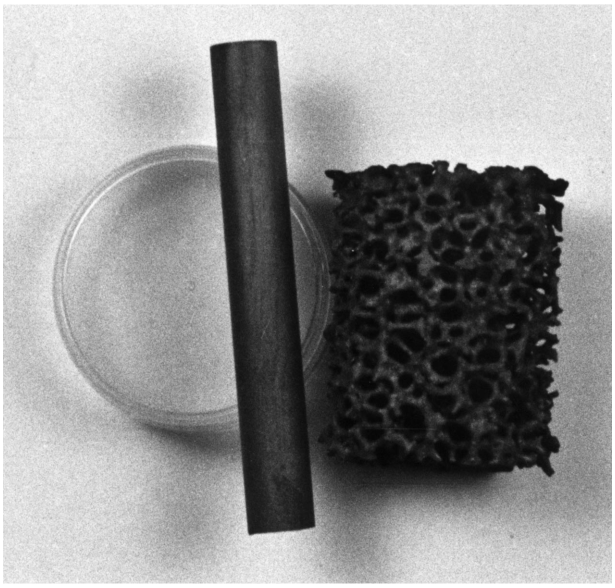


Figure 11 Ceramic foam with a coating of tantalum carbide and an alumina rod with Mo_2C coating.

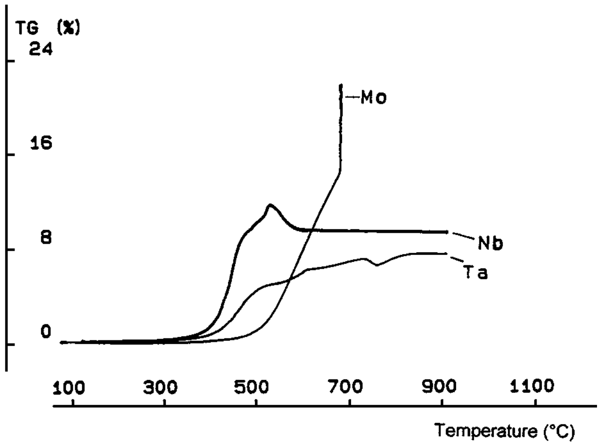


Figure 12 TGA curves of the oxidation of carbides produced at 1600 °C from NbR (a) and TaR (b), and at 1200 °C from $MoEg_1$ (c) precursor.

1600 °C (molybdenum carbide, 1200 °C), and after cooling they were reheated in air. Fig. 12 depicts TGA curves of the reheating experiments for the NbRe, TaRe and $MoEg_1$ precursors. Reheating was performed to 1000 °C with Nb and Ta products, and to 700 °C with 2 h holding at that temperature with the Mo product. These studies show that mass increase by oxidation starts for the niobium and molybdenum carbide system at approximately 300 °C and for the TaC precursors at 370 °C. Whereas the oxidation of Mo_2C clearly shows a one-step mechanism, oxidation of the other carbides proceeds in several steps running up to approximately 600 °C for NbC and up to approximately 800 °C for TaC. The reasons for these complex oxidation mechanisms are not clear. These behaviors are likely caused by differential particle sizes or by different oxidation rates at the surface and in the interior of the particles. The TGA mass decrease above 525 °C for NbC and the deeping in the TGA curve for TaC at approximately 740 °C are due to the burn-off of free carbon present in the final reaction products. The contents of free carbon determined by these TGA experiments amount to 2.2 wt % for NbC and 0.5 wt % for TaC. Summarizing these experiments, the TaC materials are of the highest stability versus air oxidation.

4. Conclusions

A synthesis process for preparing spinnable polymeric carbide precursors starting from acetylacetone derivatives of alkoxides or ethylene glycolates of transition metals Nb, Ta and Mo has been developed. It was found that acac groups in derivatives of the type $(acac)_n\ M(OR)_m$ act as chelating ligands, which slowdown the reactivity and control transesterification of the OR groups. Synthesis routes to linear polymeric precursors have been established by reaction of these derivatives with organic groups having two or more reactive OH groups and act as bridging ligands. The presence of both chelating and bridging ligands is regarded as the key for preparing spinnable carbide precursors (see also [5]).

The polymers are soluble in a lot of common solvents. Concentrated solutions exhibit the occurrence of spinnability and film production. We conclude that polymers of low molecular weight are formed in the solutions; condensation and polymerization are completed at higher temperatures and superimposed with the onset of degradation reactions. To avoid deformation, it is essential that hand-drawn fibres undergo a lengthy drying process.

Heat treatment at 1200 and 1500 °C, respectively, converts the polymer fibres into Mo_2C, NbC and TaC fibres. The resulting fibres are partially porous and brittle, and contain a low amount of free carbon. The carbon content was found to be adjustable with the amount of organic materials added to the reaction solutions. It is thought that lower heating rates and higher reaction temperatures will reduce pore generation and increase sintering phenomena in the fibres and films. Further studies are needed to clarify the optimum heating conditions. Because of their chemical and physical properties the polymer-derived carbide materials are of potential interest for use in catalysts and ceramic composites.

References

1. K. THRONE, S. J. TING, C. J. CHU, J. D. MACKENZIE, T. D. GETMAN and M. F. HAWTHORNE, *J. Mater. Sci.* **27** (1992) 4406.
2. Y. KUROKAWA, H. OTA and T. SATO, *J. Mater. Sci. Lett.* **13** (1994) 516.
3. M. NARISAWA, S. KIDA, T. SIMOO, K. OKAMURA and Y. KURACHI, *J. Sol–Gel Sci. Technol.* **4** (1995) 31.
4. H. PREISS, B. MEYER and C. OLSCHEWSKI, *J. Mater. Sci.* **33** (1997) 713.
5. H. PREISS. E. SCHIERHORN and K.-W. BRZEZINKA, *ibid.* submitted.
6. P. N. KAPOOR and R. C. MEHROTA, *J. Less-Common Metals* **8** (1965) 339.
7. R. C. MEHROTA and P. N. KAPOOR, *ibid.* **7** (1964) 176.
8. *Idem. ibid.* **7** (1984) 453.

9. B. SPIVACK and Z. DORI, *Coord. Chem. Rev.* **17** (1975) 99.
10. C. GUIZARD, N. CYGANKIEWICZ, A. LARBOT and L. COT, *J. Non-Cryst. Solids* **82** (1986) 86.
11. S. DOEUFF, M. HENRY, C. SANCHEZ and J. LIVAGE, *ibid.* **89** (1987) 206.
12. H. PREISS, D. SCHULTZE and P. KLOBES, *J. Eur. Ceram. Soc.* **17** (1997) 1423.

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