JOURNAL OF Materials CHEMISTRY

Mixed Si/C/M/O ceramics from 2,5-disilahexane/metal carbonyl (M=Fe and Co)

Stéphane Bourg, Bruno Boury and Robert J. P. Corriu*

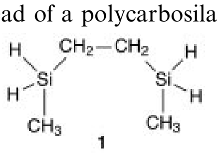
UMR 5637, CC 007, Montpellier II, Place E. Bataillon, 34095 Montpellier Cedex 5, France

Reactions of 2,5-disilahexane with cobalt or iron carbonyl were performed in order to prepare cobalt or iron organosilicon ceramic precursors. Characterization of their structure by NMR and IR spectroscopies indicates the presence of mixed oligomeric and molecular species. Pyrolysis under argon at 1000 °C gives multiphase ceramics in high yields. Part of the CO ligands were incorporated during the thermal decomposition. Materials were characterized by X-ray, Raman, TEM and magnetic susceptibility analyses. For cobalt and iron, formation of metal-rich nodules included in a homogeneous matrix is observed for the sample pyrolyzed at 1000 °C. Crystalline Fe_3Si or Co_2Si are detected and the presence of amorphous oxide or oxycarbide phases is consistent with the high oxygen level. Between 1200 °C and 1400 °C, a carbothermal reduction process occurs at different temperatures for the iron and the cobalt precursors. Elimination of CO and SiO occurs with modification of the ceramic phases. Formation of SiC and silicides (FeSi for **I** and CoSi for **II**) is observed. Melting of the Fe_3Si phase leads to the formation of spherical metallic particles.

Pyrolysis of heteroatom-containing polymers such as polycarbosilanes, polysilanes, *etc*., has been effective in the preparation of silicon carbide as reviewed recently.[1] Such preceramic polymers also might be useful as a soluble source of Si and C needed to produce other ceramics. Recent developments of this approach have shown that organometallic precursors can be envisaged for the preparation of Si/C/M phases (M= transition metal). This offers several advantages including initiation of solid state reactions under mild conditions and final form of the expected material.

Three different ways can be envisaged to introduce the metal in the material. Seyferth *et al.* developed a technology using the polymer (polymethylsilane or a polysilazane) as a binder of a transition metal powder.[2,3] Another general route consists in the pyrolysis of a polymer mixed with a complementary organometallic compound, by this way the following ceramics were obtained: SiC/TaC from polycarbosilane (PCS)[4] and tantalum ethoxide;[5] SiC/MC ceramics (M=Ti, Zr, Hf) from polymethylsilane (PMS)[6] mixed with a metallocene;[6] SiC/AlN by rapid pyrolysis of vinylic polysilane (VPS)[7] and $[R_2AlNH_2]_3$.[8] SiC/M_xN_y or SiC/MC ceramics (M=Ti, Zr, Hf, Ta, Nb, Mo, W) were prepared by thermal decomposition of a poly[(organosilylene)diacetylene] and a metal oxide.[9–11] The third general process is the pyrolysis of organometallic polymers containing both organosilicon and metal groups in their structural units.[12,13] Pyrolysis of transition metal-containing organosilicon–diacetylene oligomers gave multiphase ceramics.[14]

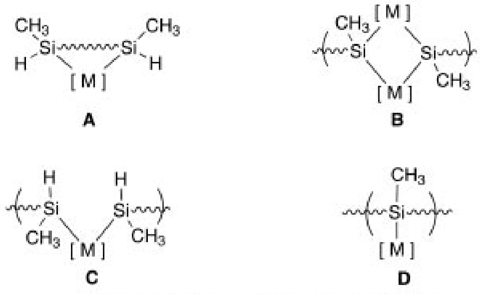
Transition metal reagents were also reported to enhance the ceramic yields of SiC preceramic precursors. Recently, we reported how 2–20% of iron pentacarbonyl or dicobalt octacarbonyl can react with polysilethylene (PSE),[15] catalyzing its thermal decomposition and increasing the final ceramic yield. During the pyrolysis, iron and cobalt are incorporated in the ceramic residue, leading to a mixed silicon carbide/metal silicide ceramic.[16–18] These studies have shown that the chemistry involved between the polymer and the transition metal catalyst can be partially controlled. We considered the possibility of improving this approach by using a molecular organosilicon compound instead of a polycarbosilane.



1

Here, our aim was to build the preceramic precursor directly starting from 2·5-disilahexane, **1**, and transition metal complex units.

Such a synthesis is based on the well known reactivity of the Si—H bond toward a metal carbonyl.[19] From the previous literature, compounds with general structure A, B, C or D are expected.

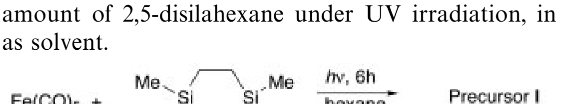


[M]=transition metal complex with (CO) ligands

Results

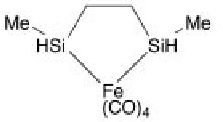
Ceramic precursor from 2,5-disilahexane/iron pentacarbonyl

Preparation of the 2,5-disilahexane/iron pentacarbonyl precursor, I. Preparation of precursor **I** was performed following eqn. (1). Iron pentacarbonyl was reacted with a stoichiometric amount of 2,5-disilahexane under UV irradiation, in hexane as solvent.



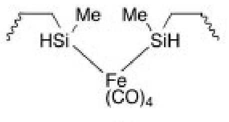
(1)

The reaction was monitored by IR spectroscopy and the irradiation stopped when the ν_{CO} bands of the initial $Fe(CO)_5$ had disappeared. The solution was filtered and the solvent removed. The oily brown residue is analyzed by IR, ^1H and ^{29}Si NMR spectroscopies. The ^{29}Si NMR spectrum shows two signals at δ 33 and 34. On a DEPTC ^{29}Si NMR spectrum, these two signals appear as doublets with $J_{Si-H}=198$ Hz and 188 Hz, respectively. They correspond to a silicon atom linked to one hydrogen atom and one iron atom.[20,21] A third signal at δ 130 can be attributed to a silicon atom linked to two iron atoms.[22] The ^1H NMR spectrum clearly indicates the presence of a Si—H function at δ 4.46. *Cis* and *trans* isomers of complex **2** and **3** can be proposed on the basis of these observations. They correspond to molecular species but polymeric structures like **4** and **5** have also to be considered. Elemental analysis of the oily product (Table 1) is consistent with the formation of **2** or **4**. However, the ^1H NMR spectrum presents also a signal at δ 16 probably due to a Fe—H bond but cannot be attributed to a well defined structure.

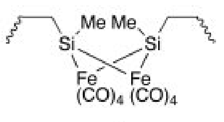


2

3



4



5

Thermal analysis. Further purification of the oily product was not intended and it was converted into a ceramic by thermal decomposition under an argon atmosphere. This transformation is monitored by thermogravimetry (TG) from 50 to 1400 °C (Fig. 1).

Between 50 and 350 °C, a mass loss of 11.2% was observed whereas the removal of all the CO ligands should lead to a mass loss of 38%. The IR spectrum of the material recovered at 400 °C does not show any carbonyl stretching vibrations. The second mass loss (8.1%) occurs between 350 and 1200 °C. A last mass loss of 17.3% due to a carbothermal reduction step, occurs between 1350 and 1400 °C. The final ceramic yield is 65%.

Table 1 Molar ratios of precursor **I** determined from elemental analyses

temperature/°C	Si	Fe	C	O	H
20	2	1.1	8.2	4.3	11.5
200	2	1.05	6.6	3.55	12.4
600	2	1.1	5.3	3.1	3.7
900	2	1.1	5.2	3.1	1.2
1400	2	1.1	3.5	1.3	0.6

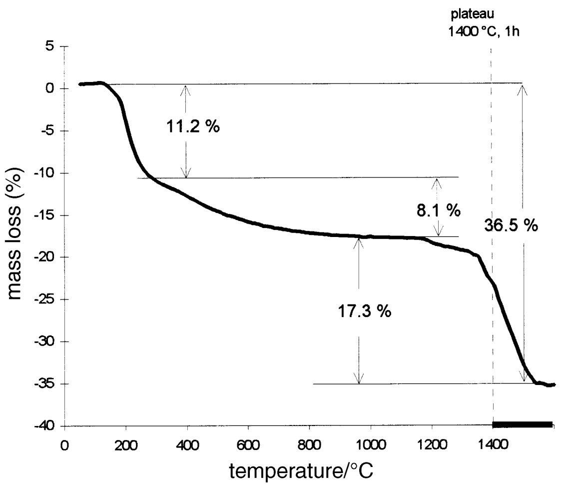


Fig. 1 TG profile of the precursor **I** pyrolyzed under argon (heat flow: 5 °C min^{-1})

Characterization of the ceramic material. Material recovered at 1000 °C is black and vitreous. Its elemental analysis presents a Fe/Si ratio similar to the precursor's one. The levels of oxygen and carbon at 1000 °C confirm that C and O were incorporated in the material during the thermal decomposition. This insertion corresponds to the reaction of 3 CO. SEM shows an homogeneous material but TEM analyses reveal the presence of 10 nm size metal-rich particles homogeneously dispersed and embedded in a matrix [Fig. 2(*a*)]. At 1000 °C, well crystallized SiC and Fe_3Si phases are detected by X-ray powder diffraction analysis [Fig. 3(*a*)].

Raman spectroscopy is used to detect and characterize the presence of free carbon.[23] Bands at 1333 and 1604 cm^{-1} are attributed to the D and G bands of graphitic carbon respectively [Fig. 4(*a*)]. The relative domain size correlates inversely with the intensity ratio of the D to G band (I_D/I_G), while the width of the G band relates to the disorder within the carbon sheets. On a 900 °C sample, the intensity ratio is 0.9 and the G bandwidth is around 55 cm^{-1}. This corresponds to an average domain size of 45 Å and a disordering similar to that of a glassy carbon.

The ceramic obtained after carbothermal reduction (1400 °C, 1 h) is a friable and heterogeneous material made of spherical metallic particles in a black matrix, mixed with a white deposit. A Si/Fe ratio of 0.33–0.5 was measured by EDS analysis in the metallic spheres. SEM shows the presence of an interfacial melting zone between a melted metal rich phase and a non-metallic domain [Fig. 2(*c*)]. TEM shows great homogeneous domains surrounded by free carbon [Fig. 2(*b*)]. X-Ray powder diffraction analysis indicates the presence of well-crystallized SiC and FeSi phases in the black powder [Fig. 3(*b*)]. Poorly crystallized SiO_2 is observed in this black powder and in the white deposit. The Raman spectrum of a 1400 °C sample

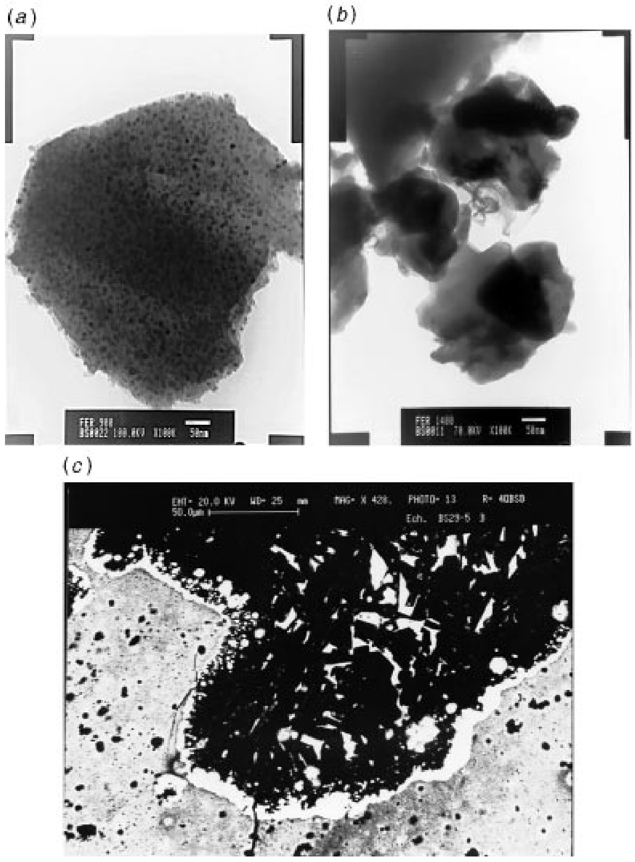


Fig. 2 Microscopy analyses of precursor **I**: (*a*) TEM photograph of a 900 °C sample; (*b*) TEM photograph of a spherical metallic particle found in a 1400 °C sample; (*c*) BEI photograph of an interfacial melting zone observed in a 1400 °C sample

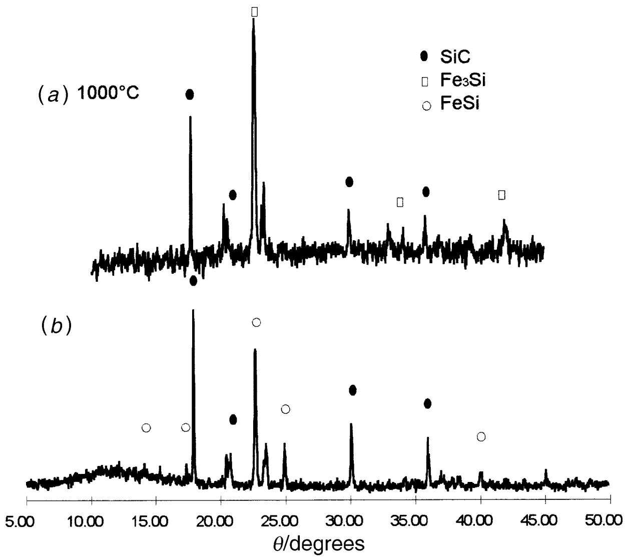


Fig. 3 XRD patterns of the residues resulting from the pyrolysis of precursor **I**: (*a*) 1000 °C sample; (*b*) 1400 °C sample

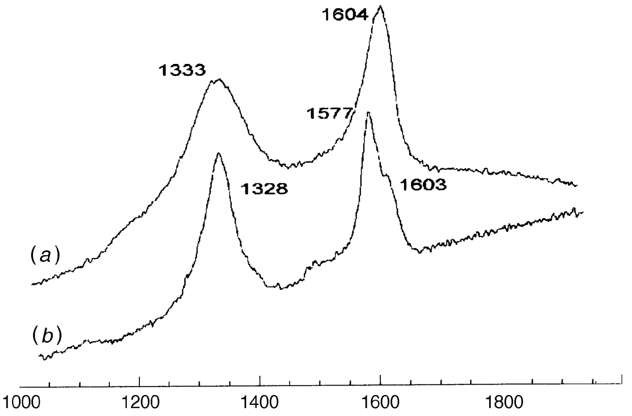


Fig. 4 Raman spectra of the residues resulting from the pyrolysis of precursor **I**: (*a*) 900 °C sample; (*b*) 1400 °C sample

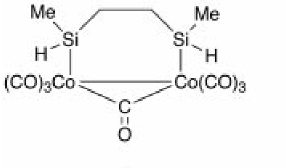
presents two bands at 1328 and 1577 cm^{-1}. This latter band has a shoulder at 1603 cm^{-1} [Fig. 4(*b*)]. $I_D/I_G = 0.9$ and the G bandwidth is *ca.* 60 cm^{-1}. The sample corresponds to a glassy carbon similar to the 900 °C sample.

Ceramic from 2,5-disilahexane/cobalt carbonyl, precursor II

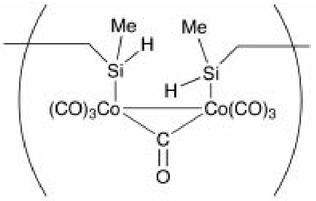
Preparation of the 2,5-disilahexane/cobalt carbonyl, precursor II. Preparation of precursor **II** was performed following eqn. (2). Equimolar amounts of 2,5-disilahexane, **1**, and dicobalt octacarbonyl are reacted by simply mixing the two products in hexane at room temperature.

$$Co_2(CO)_8 + MeSiH_2CH_2CH_2SiH_2Me \xrightarrow[\text{hexane}]{\text{24h}} \text{Precursor II} \qquad (2)$$

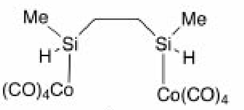
After removal of the solvent, precursor **II** was obtained as a viscous oil in quantitative yield, assuming that all the Si and Co atoms remained in the precursor. The ^{1}H NMR spectrum shows a broad signal at δ 3.36, showing that the Si—H bonds are not totally lost during this reaction. Signals due to hydrogen atoms bonded to cobalt atoms, expected for Si—H···Co or Si···H—Co species between δ 0 and −15, are not observed.[24–27] The ^{29}Si NMR spectrum shows three signals at δ 60.5, 57.2 and 45.8 characteristic of ≡Si—Co species. No signals corresponding to —SiH$_2$— groups were observed around δ −25 to −30. The major signal, at δ 60.5 is attributed to **6** or **7** and the signal at δ 45.8 to **8**.[21] Structures like **6** or **7** are also confirmed by IR analysis which showed bridging CO ligands ($\nu_{CO} = 1835$ cm^{-1}), monodentate CO ligands ($\nu_{CO} = 1970$–2070 cm^{-1}) and Si—H bonds ($\nu_{SiH} = 2120$ cm^{-1}) different from the SiH$_2$ of the starting material ($\nu_{SiH} = 2132$ cm^{-1}).



6



7



8

This reaction was also performed using silane/Co$_2$(CO)$_8$ ratios of 2 and 0.5 in order to prepare preceramic compounds with various Si/Co ratios. When an excess of **1** is used, it remained unreacted and was lost on removal of the solvent. On the other hand, when an excess of Co$_2$(CO)$_8$ is added, formation of Co$_4$(CO)$_{12}$ was observed.

Thermal analysis. Precursor **II** was converted into a ceramic using the experimental conditions described for precursor **I**. TG analysis (Fig. 5) shows a first mass loss of 30% between 100 and 300 °C. In this range of temperature, decomposition of the carbonyl complexes and elimination of the CO ligand is expected but it should correspond to a mass loss of 50%. The experimental result indicates that, as for precursor **I**, half of the CO ligands react with the other elements of the precursor, leading to the incorporation of C and O in the residue. At higher temperature, two other mass losses occur, from 300 to 700 °C (7.5%) and from 1200 to 1400 °C (13%). The latter is attributed to a carbothermal reduction step. The final ceramic yield is 49%, no transformation being observed from 1400 to 1600 °C.

Characterization of the ceramic material. When the final temperature of pyrolysis is between 800 and 1000 °C, the ceramic is a black, homogeneous material. Elemental analyses show high levels of oxygen and carbon, O/Si = 1.5 and C/Si = 2.4. In addition, the Co/Si ratio is lower than in the starting precursor: 0.73 *cf.* 1.08. Thus, elimination of volatile cobalt

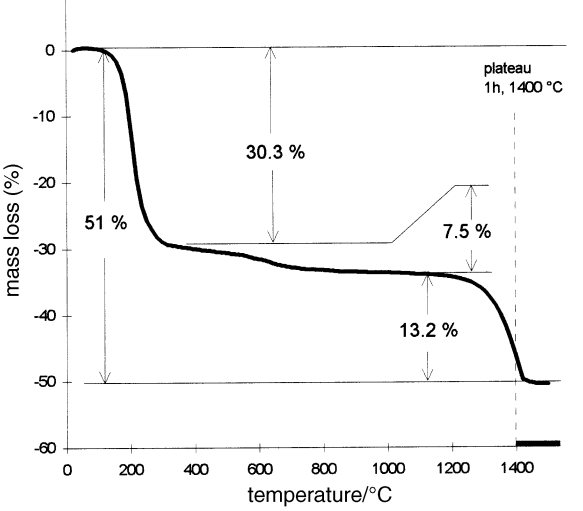


Fig. 5 TG profile of the precursor **II** pyrolyzed under argon (heat flow: 5 °C min^{-1})

Table 2 Molar ratios of precursor **II** determined from elemental analyses

temperature/°C	Si	Co	C	O	H
20	2	2.16	12.9	8.8[a]	14.3
200	2	1.8	6.8	2.9	14.0
400	2	1.64	5.8	2.9	9.4
900	2	1.46	4.74	3.08	<0.5
1400	2	1.8	3.72	2.45	<0.5

[a] Given as difference from 100% because direct measurement is not possible on such a material.

derivatives during the thermal decomposition has to be considered. TEM analysis reveals the presence of spherical particles homogeneously dispersed and embedded in a matrix. The size of these particles increases with the final temperature of pyrolysis, from 5 nm at 800 °C to 20 nm at 1000 °C [Fig. 6(*a*)]. X-Ray diffraction analysis of a 1000 °C sample shows a poorly crystallized Co_2Si phase but the crystal size could not be determined and no SiC phase was observed [Fig. 7(*a*)]. By measurement of the magnetic susceptibility of a 900 °C sample from 20 to 800 °C (Fig. 8), an inflection point at *ca.* 720 °C and the persistence of a susceptibility above 750 °C is consistent with the presence of [Co_xSi_y; ($0.1 < x < 0.88$ and $x + y = 1$)] phases which have a Curie point between 1100 and 724 °C.[28]

The Raman spectrum of a 900 °C sample shows two bands at 1358 and 1590 cm^{-1}, attributed to the D and G bands of graphitic carbon respectively [Fig. 9(*a*)]; $I_D/I_G = 1.1$ and the G bandwidth is *ca.* 60 cm^{-1}. This corresponds to an average domain size of 40 Å and a disordering similar to that of a glassy carbon.

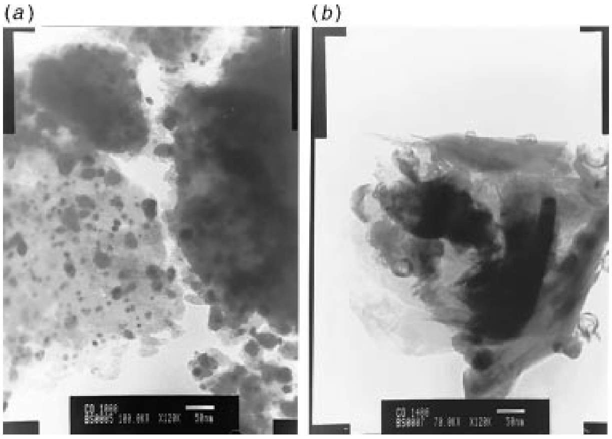


Fig. 6 TEM photographs of the residues resulting from the pyrolysis of precursor **II**: (*a*) 1000 °C sample; (*b*) 1400 °C sample

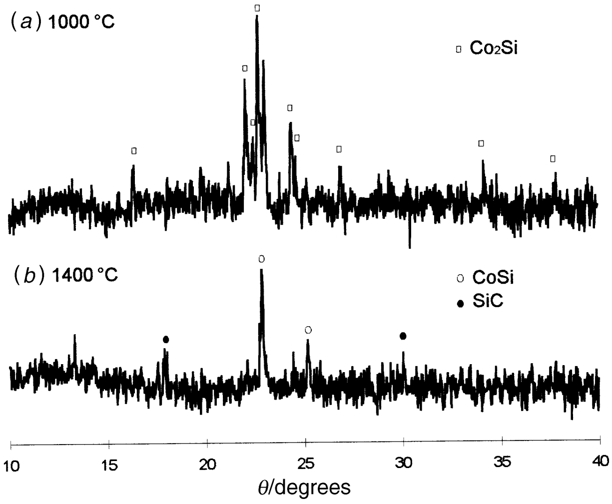


Fig. 7 XRD patterns of the residues resulting from the pyrolysis of precursor **II**: (*a*) 1000 °C sample; (*b*) 1400 °C sample

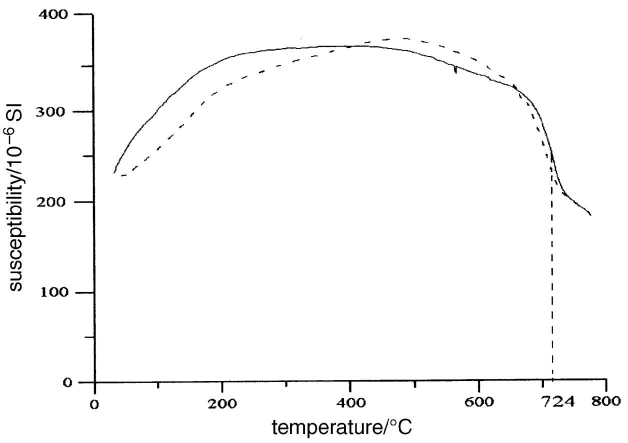


Fig. 8 Measurement of the magnetic susceptibility of the residues resulting from the pyrolysis of precursor **II** pyrolyzed at 900 °C: (—) heating curve and (---) cooling curve

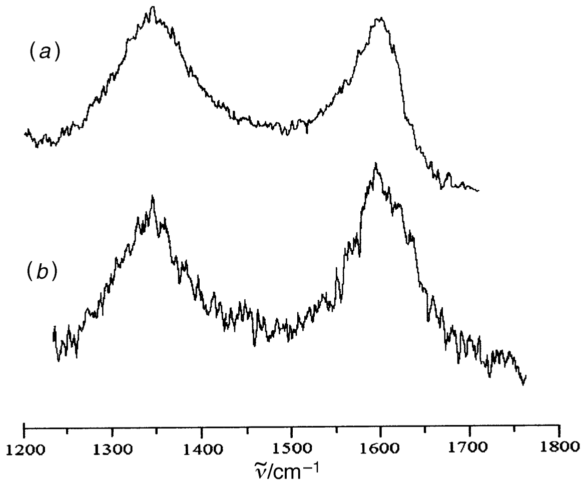


Fig. 9 Raman spectra of the residues resulting from the pyrolysis of precursor **II**: (*a*) 900 °C sample; (*b*) 1400 °C sample

After carbothermal reduction, a black friable material mixed with a white deposit was recovered. X-Ray powder diffraction analysis shows poorly crystallized CoSi and SiC phases (with very small crystal size) in the black material and SiO_2 in the white deposit [Fig. 7(*b*)]. No metallic cobalt was detected. TEM photographs of the black material show different large homogeneous domains and carbon layers [Fig. 6(*b*)]. The Raman spectrum of this sample presents two bands at 1350 and 1580 cm^{-1} [Fig. 9(*b*)]. $I_D/I_G = 0.8$ and the G bandwidth is *ca.* 70 cm^{-1}. An average domain size of 50 Å is observed with a disordering similar to that of the 900 °C sample. The specific surface area of the material is 100 $m^2\ g^{-1}$ before and 50 $m^2\ g^{-1}$ after carbothermal reduction.

Discussion

Structure of the precursors

Soluble Si/C/M/O ceramic precursors were prepared from 2,5-disilahexane and iron or cobalt carbonyl (M=Fe, Co). The reaction of the initial Si—H bonds with the metal reagent by intra- or inter-molecular reactions results in the formation of Si—M bonds in monomeric or oligomeric structures. This result is quite unexpected because the four Si—H functions of the 2,5-disilahexane could lead to the formation of four Si—M bonds.[19] It would lead to a bridging of the 2,5-disilahexane units by iron or cobalt carbonyl entities, resulting in an insoluble polymeric network or, at least, to a very complicated mixture of oligomers. Indeed, the reactivity of the Si—H bond has been used to cross-link polymeric ceramic precursors.[2,18,29] Our results suggest that under mild conditions (0.1 M, room temperature, 24 h), the reaction of the Si—H bond can be limited. Therefore it is possible to form iron or cobalt complexes with remaining Si—H functions. In precursors **I** and **II**, the silicon atoms are assumed to be linked mainly to only one transition metal center as evidenced by ^{29}Si NMR spectroscopy. Elemental analyses and IR spectroscopy confirm that the major compound present in both precursors contains an average of one Si—H bond per silicon atom.

Thermal transformation

The persistence of reactive Si—H bonds probably allows the thermal cross-linking of the precursor between 50 and 300 °C. Species with two Si—M bonds (M = Co, Fe) are assumed to be formed and serve to further cross-link the material. From previous literature, the first important mass loss is attributed to the decomposition of the metal carbonyl moiety, leading to the elimination of CO ligands. However, half of them react by another process which results in the incorporation of carbon and oxygen in the resulting ceramic. The chemistry occurring in this process remains unclear. Indeed, elimination of the CO can lead to the formation of cobalt clusters or insertion of Co in Si—C, C—C or C—H bonds.[30] Mechanisms based on the formation of silylene species and Si—Si bonds, followed by Kumada rearrangement, were also proposed for the thermal decomposition of polysilethylene with a catalytic amount of metal carbonyl.[18,29] Solid state NMR experiments were not useful owing to the ferromagnetic properties of the samples.

Further heating of precursors **I** and **II** from 300 to 1000 °C leads to a limited mass loss. From elemental analyses, it is assumed to arise from the evolution of hydrogen and organic fragments. Similar results were observed for polysilethylene precursors and were interpreted as thermal homolytic cleavage of the Si—C and C—H bonds. The increase of the Si/Co ratio between 400 and 900 °C implies the elimination of volatile Co species from precursor **II**, possibly $HCo(CO)_4$ as it was reported during the decomposition of cobalt complexes.[31]

Structure of the ceramics at 1000 and 1400 °C

For precursors **I** and **II**, formation of metal-rich nodules included in a homogeneous matrix is observed in 1000 °C samples. However, the size of the nodules remains unchanged for iron while it increases with cobalt. For both metals, silicide like Fe_3Si, FeSi, $FeSi_2$ and Co_2Si, CoSi, $CoSi_2$ are well known but only Fe_3Si and Co_2Si are effectively detected. Silicide with $M/Si < 1$ were expected because precursors **I** and **II** are silicon rich and the standard enthalpies of formation of Fe_3Si and $FeSi_2$ or Co_2Si and $CoSi_2$ are similar (Table 3).[28]

It thus appears that despite the initial homogeneous dispersion of metal, silicon and carbon atoms in the precursors, thermodynamically stable phases are formed. Similar results were reported for other preceramic polymers doped with iron or cobalt derivatives.[14,16] Surprisingly, silicon carbide is present in ceramic **I** but not in **II**. These results cannot be interpreted at this time because both cobalt and iron are known to promote the crystallization of SiC[17,18] and were also found to react with SiC from 900 °C to give carbon and mixtures of various silicides.[32,33] It can be assumed that oxygen is incorporated in an amorphous oxide or oxycarbide phase. Characterized phases in pyrolyzed precursors **I** and **II** are given in Table 4.

Table 3 Experimental values of ΔH°_{298} for iron and cobalt silicides[24]

silicides	ΔH°_{298}/kJ mol^{-1}
Fe_3Si	−25.8
FeSi	−39.3
$FeSi_2$	−30.6
Co_2Si	−38.5
CoSi	−50.2
$CoSi_2$	−34.3

Table 4 Characterized phases in pyrolyzed precursor **I** and **II**

precursor	before carboreduction (1000 °C)	after carboreduction (1400 °C)
I	SiC^a, $Fe_3Si_{(f)}{}^a$	SiC^a, $FeSi^a$, C^c, $SiO_2{}^{a,b}$
II	$ss[Co_{0.88}Si_{0.12}]_{(f)}Co_2Si^a$, C^d	SiC^a, $CoSi^a$, $SiO_2{}^{a,b}$, $C^{c,d}$

[a]X-Ray analysis. [b]SEM. [c]TEM. [d]Raman. *(f)* ferromagnetic, ss: solid solution.

Table 5 Elemental analyses of precursor **I** after pyrolysis

temperature/°C	Si	Fe	C	O	H
20	19.1	20.3	31.0	23.2	3.9
200	20.3	21.3	28.9	20.7	4.5
600	23.6	25.6	26.7	21.0	1.6
900	22.8	25.8	25.2	20.2	0.5
1400	30.6	34.1	22.8	11.8	<0.3

Table 6 Elemental analyses of precursor **II** after pyrolysis

temperature/°C	Si	Co	C	O	H
20	11.3	25.8	31.4	—	2.9
200	16.4	30.6	24.2	14.0	4.1
400	18.5	32.1	23.1	15.5	3.1
900	21.8	33.6	22.2	19.3	<0.3
1400	22.0	42.3	17.7	15.6	<0.53

The mass loss observed at 1350 °C for precursor **I** and 1250 °C for precursor **II** results from carbothermal reduction. Elimination of CO leads to a decrease of the level of carbon and oxygen in the ceramic residues. In both cases, we observe the formation of a SiO_2 phase, probably due to the decomposition of SiO, a very reactive gas which has already been reported in the carbothermal reduction process of Si/O/C preceramic polymers.[34,35]

For **I**, the carbothermal reduction occurs at 1350 °C, higher than the melting point of the Fe_3Si phase, leading to the formation of metallic spherical particles with an average composition between Fe_2Si and Fe_3Si (mp Fe_3Si *ca.* 1250 °C, mp FeSi 1410 °C, mp $FeSi_2$ 1220 °C). The same behavior is not observed for **II** because the carbothermal reduction occurs before the melting of the cobalt silicide phase (mp Co_2Si 1332 °C, mp CoSi 1480 °C, mp $CoSi_2$ 1326 °C). In both cases, we observe the formation of SiC and silicide like FeSi for **I** and CoSi for **II**. Finally, we found that formation of cobalt or iron metal was not detected by X-ray analysis. Formation of crystallized metallic oxide phases is not observed at 1000 or 1400 °C whereas iron oxides (Fe_2O_3 and FeO) or cobalt oxide (CoO) are stable phases. At this time, the complexity of this behavior is the major limitation for a complete interpretation of the processes.

Conclusion

We found that the reaction between an organosilicon compound with four Si—H bonds and a transition metal reagent can be limited. The resulting mixture of molecular and oligomeric complexes is useful for the preparation of Si/M/C/O ceramics (M=Fe, Co). When the precursors have CO ligands on the metal, incorporation of oxygen and carbon occurs during their thermal decomposition. These precursors allow the formation at 800–1000 °C of nanocomposites characterized as homogeneous dispersions of metallic silicide nodules in amorphous matrices. Above 1200 °C, a carbothermal reduction process leads to partial elimination of the excess of carbon and oxygen introduced initially by the reaction of the CO ligands. We found that starting from a homogeneous dispersion at the atomic level of silicon, carbon and metal results in a mixture of thermodynamically stable phases: metal silicides, silicon carbide, silica and carbon.

Experimental

All the reactions were carried out under an atmosphere of dry argon. Solvents were dried using standard techniques. IR spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer. NMR spectra were obtained with a Bruker Advance DPX 200 (^{1}H, ^{13}C) or a Bruker WP 200 SY (^{29}Si), solvent $CDCl_3$ or C_6D_6 with TMS as an internal standard. Pyrolyses were performed with Eurotherm or Carbolite furnaces. The heating rate was 5 °C min^{-1}. Thermogravimetry was performed on a Netzsch STA 409 Thermobalance under an argon atmosphere. The heating rate was 5 °C min^{-1}. Elemental analyses were performed at the Service Central d'Analyses du CNRS at Vernaison, France. Elemental analyses (%) for the iron and cobalt derived samples are given in Tables 5 and 6, respectively. Raman spectra were recorded on a Dilor RT 30 spectrometer, at 488 nm. Specific surface areas were measured on a Micromeretics Gemini III. Magnetic susceptibility experiments were measured on a Bartington MS 2 susceptibilimeter, at 10^{-4} Torr, with a heating rate of 5 °C min^{-1}. X-Ray diffraction measurements were obtained using Cu-Kα radiation on a Phillips Diffractometer. SEM was performed on a LEICA S 360 Cambridge at 20 kV and TEM was performed on a JEOL 1200 EX2 at 100 kV.

The synthesis of 2,5-disilahexane **1** was detailed in our previous communication.[36]

Precursor I

In a quartz reactor, **1** (3.54 g, 30 mmol) and $Fe(CO)_5$ (5.88 g, 30 mmol) were mixed in 800 ml of hexane. Under magnetic stirring, the mixture was irradiated for 6 h with a 450 W mercury lamp. A cooling system maintained the temperature between 25 and 30 °C. The reactor was emptied, washed and dried carefully at 90 min intervals. After irradiation was ceased, the mixture was filtered to remove decomposition products. Removal of the solvent under vacuum gave 7.56 g of crude product (90%). Owing to paramagnetism of the solution, ^{1}H NMR spectroscopy gave only broad signals. ^{1}H (C_6D_6) δ 4.47, 1.36, 0.92, 0.47, 0.41, 0.30, −16.20. ^{29}Si NMR (C_6D_6) δ 130.59, 34.06 ($J_{Si-H}=198$ Hz), 32.99 ($J_{Si-H}=188$ Hz). IR (hexane, cm^{-1}) 2095w, 2067, 2048w, 2038, 2025, 2009, 1999, 1985, 1970. Elemental analysis is given in Table 5.

Precursor II

2,5-Disilahexane (295 mg, 2.5 mmol) was added dropwise to a solution of dicobalt octacarbonyl (855 mg, 2.5 mmol) in 25 ml of hexane. The mixture was stirred for 24 h at room temperature and filtered quickly through Celite. The solution was concentrated and the crude product kept at −20 °C. ^{1}H NMR spectroscopy gave only very broad signals (C_6D_6) δ 3.36, 1.23, 0.88, 0.29. ^{13}C NMR (C_6D_6) δ 206.35, 198.98, 196.82, 16.32, 6.95, −2.79. ^{29}Si NMR (C_6D_6) δ 60.50, 57.25, 48.84. IR (hexane, cm^{-1}) 2120, 2091, 2072, 2054, 2028.5, 1990, 1835. Elemental analysis is given in Table 6.

References

1 M. Birot, J. P. Pillot and J. Dunoguès, *Chem. Rev.*, 1995, **95**, 1443.
2 D. Seyferth, H. Lang, C. A. Sobon, J. Borm, H. J. Tracy and N. Bryson, *J. Inorg. Org. Polym.*, 1992, **2**, 59.
3 D. Seyferth and G. H. Wieseman, *J. Am. Ceram. Soc.*, 1984, **67**, C.
4 S. Yajima, J. Hayashi and M. Omori, *Chem. Lett.*, 1975, 931.
5 K. Thorne, E. Liimatta and J. D. Mackenzie, *J. Mater. Res.*, 1991, **6**, 2199.
6 D. Seyferth, in *Silicon based polymer science. A comprehensive resource*, ed. J. M. Ziegler and F. W. G. Fearon, American Chemical Society, Washington, DC, 1990, ch. 31.
7 C. L. Schilling, J. P. Wesson and T. C. Williams, *Am. Ceram. Soc. Bull.*, 1983, **62**, 912.
8 C. L. Czekaj, M. L. Hackney, W. J. Hurley, L. V. Interrante and G. A. Siegel, *J. Am. Ceram. Soc.*, 1990, **73**, 352.
9 R. J. P. Corriu, P. Gerbier, C. Guerin and B. Henner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1195.
10 R. J. P. Corriu, P. Gerbier, C. Guerin, and B. Henner, in *Silicon-Containing Polymers*, ed. R. G. Jones, Royal Society of Chemistry, Cambridge, 1995, p. 3.
11 R. J. P. Corriu, P. Gerbier, C. Guerin and B. Henner, in *Applications of the Organometallic Chemistry in the Preparation and Processing of Advanced Materials*, ed. F. H. Harrod and R. M. Laine, Kluwer Academic, London, 1995, p. 203.
12 B. J. Aylett and H. M. Colquhoun, *J. Chem. Soc., Dalton Trans.*, 1977, 2058.
13 B. Z. Tang, R. Petersen, D. A. Foucher, A. Lough, N. Coombs, R. Sodhi and I. Manners, *J. Chem. Soc., Chem. Commun.*, 1993, 523.
14 R. J. P. Corriu, N. Devylder, C. Guerin, B. Henner and A. Jean, *J. Organomet. Chem.*, 1996, **509**, 249.
15 B. Boury, R. J. P. Corriu and L. Carpenter, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 785.
16 S. Huille, Thèse de l'Université Montpellier II, 1993.
17 L. Lutsen, Thèse de l'Université Montpellier II, 1994.
18 R. J. P. Corriu, M. Enders, S. Huille, L. Lutsen and J. E. Moreau, in *Applications of the Organometallic Chemistry in the Preparation and Processing of Advanced Materials*, ed. F. H. Harrod and R. M. Laine, Kluwer Academic, London, 1995, p. 185.
19 T. D. Tilley, in *The Silicon–Heteroatom Bond*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1991, p. 245.
20 G. Bellachioma, G. Cardaci, E. Colomer, R. J. P. Corriu and A. Vioux, *Inorg. Chem.*, 1989, **28**, 519.
21 L. Vancea and W. A. G. Graham, *Inorg. Chem.*, 1974, **13**, 511.
22 C. P. S. Bhanu, R. J. P. Corriu and G. Lanneau, *Organometallics*, 1995, **14**, 1657.
23 D. S. Knight and W. B. White, *J. Mater. Res.*, 1989, **4**, 385.
24 U. Schubert, J. Müller and H. G. Alt, *Organometallics*, 1987, **6**, 469.
25 M. Cowie and M. J. Bennett, *Inorg. Chem*, 1977, **16**, 2321.
26 E. Colomer, R. J. P. Corriu, C. Marzin and A. Vioux, *Inorg. Chem.*, 1982, **21**, 369.
27 M. J. Bennett and K. A. Simpson, *J. Am. Chem. Soc.*, 1971, **93**, 7156.
28 M. E. Schlesinger, *Chem. Rev.*, 1990, **90**, 607.
29 R. J. P. Corriu, S. Huille and J. J. E. Moreau, *Chem. Mater.*, 1994, **15**, 6.
30 J. P. Collman, L. S. Hegedus and R. G. Norton, in *Principles and Applications of Organotransition Metal Chemistry*, Mill Valley, CA, 1987.
31 R. B. King, *Adv. Organomet. Chem.*, 1964, **2**, 157.
32 T. C. Chou and J. Wadsworth, *J. Mater. Res.*, 1991, **6**, 796.
33 Y. Pan and J. L. Baptista, *J. Am. Ceram. Soc.*, 1996, **79**, 2017.
34 N. Klinger, E. L. Strauss and K. L. Komarek, *J. Am. Ceram. Soc.*, 1966, **49**, 369.
35 J. J. Biernacki and J. Wotzak, *J. Am. Ceram. Soc.*, 1989, **72**, 122.
36 S. Bourg, B. Boury, F. Carre and R. J. P. Corriu, *Organometallics*, 1997, **16**, 3097.

Paper 7/08101D; *Received* 11*th November*, 1997