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Synthesis and Characterization of SiC/MC/C Ceramics (M = Ti, Zr, Hf) Starting from Totally Non-oxidic Precursors

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The reaction of poly(dimethylsilane) (PDMS) and poly(dimethylcarbosilane) (PCS) with bis(cyclopentadienyl)M dichloride Cp_2MCl_2 (M = Ti, Zr, Hf) complexes has been used as a new route to obtain ceramic materials based on SiC-containing M. The reaction is completed at a relatively low temperature, 900 °C, yielding the corresponding amorphous SiC/MC ceramics which have been characterized by means of ^{29}Si MAS NMR. These amorphous materials have been treated at higher temperatures, 1350 °C, under a purified argon atmosphere, yielding partially crystallized products which have been studied by X-ray powder diffraction and ^{29}Si MAS NMR. The effect of the composition of the mixture of precursors is also studied in this work.

Introduction

During the past decades, the design of new precursor systems of high performance non-oxide ceramics has been a focus of considerable attention. In this way, SiC-, Si_3N_4-, or Si/C/N-based materials have been prepared by pyrolysis of organosilicon precursors.[1]

Introduction of transition metals in these non-oxide ceramic materials to improve their chemical and mechanical properties or to provide new optical and magnetic properties is an interesting goal.

To date, different approaches have been designed to obtain this type of material. On one hand, the pyrolysis of an organosilicon polymer in the presence of a metal oxide has been used as a way to obtain SiC−MC ceramics.[2] On the other hand, formation of polytitanocarbosilane (PTC) from a mixture of PDMS and titanium tetraisopropoxide and its conversion into ceramic materials has been described.[3] In this line, condensation reaction of PCS and titanium tetralkoxide has also been published.[4] More recently, it has also been reported that reaction of PCS with zirconium(IV) acetylacetonate yields polyzirconocarbosilane which can be used as precursor of Si−Zr−C−O ceramic fibers of high tensile strength at high temperature.[5]

In some cases, small amounts of polynuclear metal carbonyls have been used to facilitate the cross-link of Si−H bonds containing organosilicon polymers.[6] Compounds such as (η^5-C_5H_5)$TiMe_2$ or (η^5-C_5H_5)$TiCl_2$/*n*-BuLi have also been used as catalytic agents on the dehydrogenative polycondensation of Si−H groups of 1,4-disilapentane[7] and related polysilanes. In these cases, titanium complexes are introduced in catalytic amounts and eliminated during the process, so that finally titanium-free samples have been obtained.

So only a small number of molecular precursors, all of them containing oxygen, such as metal alkoxides or acetylacetonates, have been used to date. We proposed in our work to study the role of bis(cyclopentadienyl)−metal complexes as a new alternative source of metal to obtain Si/C/M ceramics and we report here our first results about the reactivity of bis(cyclopentadienyl)M dichloride (M = Ti, Zr, Hf) versus PDMS and PCS and their application to the synthesis of new ceramics based on Si/C/M (M = Ti, Zr, Hf). Although Cp_2MCl_2 could also act as a catalyzer of the dehydrogenation processes associated with the chain cross-link, our interest is to study the behavior of these complexes as reactants which incorporate the metal to the final ceramic materials.

Experimental Section

Synthesis. *M_xCS_y900 Series.* Syntheses of ceramic materials were performed by pyrolysis of a mixture of precursors under an argon atmosphere according to the following general procedure.

PDMS, $-(-Si(CH_3)_2-)_n-$, prepared according to the Yajima's procedure,[8] was placed in a two-necked quartz tube as the reaction vessel, which was equipped with a reflux condenser. The tube was introduced in a vertical electric furnace

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Table 1. Pyrolysis of PDMS/Cp_2MCl_2 Precursors at 900 °C for 1 h (M_xCS_y900)

name	precursor mixture (weight ratio)	Si/M molar ratio precursor	Si/M molar ratio^a ceramics	ceramic yield^b (%)	free C (%)	empirical formula ceramics
T_2CS900	1PDMS:2Cp_2TiCl_2	2.15	0.9	34.8	49.40	$TiSi_{0.9}C_{12.9}$
TCS900	1PDMS:1Cp_2TiCl_2	4.3	3.6	30.5	28.68	$TiSi_{3.6}C_{14.5}$
$TCS_{1.5}900$	1.5PDMS:1Cp_2TiCl_2	6.5	5.6	25.0	20.46	$TiSi_{5.6}C_{15.1}$
TCS_2900	2PDMS:1Cp_2TiCl_2	8.6	7.6	19.5	16.80	$TiSi_{7.6}C_{16.8}$
Z_2CS900	1PDMS:2Cp_2ZrCl_2	2.5	1.3	29.0	49.43	$ZrSi_{1.3}C_{19.4}$
ZCS900	1PDMS:1Cp_2ZrCl_2	5.0	4.0	27.2	27.83	$ZrSi_{4.0}C_{15.1}$
$ZCS_{1.5}900$	1.5PDMS:1Cp_2ZrCl_2	7.5	6.4	25.6	19.16	$ZrSi_{6.4}C_{15.6}$
ZCS_2900	2PDMS:1Cp_2ZrCl_2	10.0	8.9	23.7	16.44	$ZrSi_{8.9}C_{17.8}$
HCS900	1PDMS:1Cp_2HfCl_2	6.5	5.2	20.6	26.72	$HfSi_{5.2}C_{19.1}$

^{a} Data obtained by electron probe microanalysis. ^{b} Ceramic yield = (weight of pyrolysis residue × 100) (weight of precursor mixture)$^{-1}$ at 900 °C.

Table 2. Pyrolysis of (M_xCS_y900) at 1350 °C for 1 h (M_xCS_y1350)

name	Si/M molar ratio^a ceramics	ceramic yield^b (%)	free C (%)	empirical formula ceramics
$T_2CS1350$	1.0	68.7	47.68	$TiSi_{1.0}C_{9.6}$
TCS1350	3.5	66.1	25.70	$TiSi_{3.5}C_{10.3}$
$TCS_{1.5}1350$	5.7	70.5	18.00	$TiSi_{5.7}C_{12.0}$
TCS_21350	7.7	72.6	15.36	$TiSi_{7.7}C_{14.3}$
$Z_2CS1350$	1.2	68.3	46.62	$ZrSi_{1.2}C_{13.3}$
ZCS1350	4.2	80.7	24.87	$ZrSi_{4.2}C_{12.5}$
$ZCS_{1.5}1350$	6.6	83.8	16.78	$ZrSi_{6.6}C_{13.6}$
ZCS_21350	9.0	89.9	14.55	$ZrSi_{9.0}C_{16.6}$
HCS1350	5.4	86.5	23.91	$HfSi_{5.4}C_{16.8}$

^{a} Data obtained by electron probe microanalysis. ^{b} Ceramic yield = (weight of pyrolysis residue × 100) (weight of M_xCS_y900)$^{-1}$ at 1350 °C.

and, after the air was replaced with purified argon, PDMS was heated to 320 °C. The liquid was refluxed at this temperature for 5 h and then heated at 470 °C for 2 h. With this thermal treatment the conversion of PDMS into PCS, $-(-[Si(CH_3)H]-CH_2-)_n-$, was completed.[9a] Upon cooling to room temperature, Cp_2MCl_2 was added to the tube under argon. Then, the mixture was heated at 900 °C for 1 h, the argon atmosphere being maintained until the experiment was finished. In all the heat treatments the heating rate was 5 °C min^{-1}. Upon cooling at room temperature, the part of Cp_2MCl_2 which sublimated and condensed on the cool parts of the tube was extracted with chloroform. The remaining black solid was washed first with chloroform and then with hexane, resulting in a glossy black solid in all cases.

We have worked with different relative amounts of precursors (PDMS and Cp_2MCl_2, M = Ti, Zr, Hf) to obtain final silicon carbide based ceramic materials with variable contents on metal, following the above general procedure. Table 1 summarizes compositions prepared as well as yielding and compositions of the ceramics obtained after heat treatment at 900 °C. Samples were labeled as M_xCS_y900, where M = T (for Ti), Z (for Zr), and H (for Hf) and x and y are the weight proportions used.

M_xCS_y1350 Series. Weighed samples (0.3−0.5 g) of M_xCS_y-900 were heated in an aluminum oxide boat with a gastight aluminum oxide tube connected to a vacuum line, in a cylindrical furnace at 1350 °C for 2 h under an argon flow (heating rate of 5 °C min^{-1} up to 900 °C and 1 °C min^{-1} from 900 to 1350 °C). Pyrolysis experiments were carried out under an argon flow maintained at about 50 mLmin^{-1}. The argon was previously purified to avoid the oxygen contamination. Products obtained after thermal treatment were glossy-black powders of similar appearance to those obtained at 900 °C and were labeled as M_xCS_y1350. Yielding as well as compositions for these materials are summarized in Table 2.

Characterization Techniques. *Thermal Analysis.* Thermal behavior of Cp_2MCl_2 and PDMS or PCS mixtures has been studied by thermogravimetric analysis (TGA) on a Perkin-Elmer TGA7 instrument up to 1400 °C at a heating rate of 2 °C min^{-1} under an argon flow of 50 mL min^{-1}.

Nuclear Magnetic Resonance (NMR) Experiments. ^{29}Si and ^{13}C MAS NMR spectra of powder samples were recorded on a Varian Unity-300 spectrometer operating at 300 MHz. An MAS probe was tuned at 59.60 kHz for silicon and 75.43 kHz for carbon. Samples were packed into a zirconium oxide bearing rotor. Spinning rates of 4 kHz were used for all spectra. Chemical shifts were measured relative to tetramethylsilane (TMS). Spectra were obtained by using a 90° pulse with delays of 60 s for ^{29}Si and 10 s for ^{13}C.

X-ray Diffraction. Powder X-ray diffraction patterns were obtained with a Seifert C-3000 $\theta-\theta$ automated diffractometer, using graphite-monochromated Cu Kα radiation. Powder samples were sprinkled on a glass slide. Patterns were collected with a scanning step of 0.05° (2θ) over the angular range 15°−85° (2θ) with a collection time of 5 s step^{-1}. In addition, we have estimated the SiC/MC ratios in samples synthesized at 1350 °C, from the XRD patterns, by means of peak area measurement. For it, we prepared from commercial products (Aldrich) several SiC/MC (M = Ti, Zr, Hf) mixtures with different ratios as calibration standards.

Infrared Spectroscopy. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Perkin-Elmer FT1750 spectrometer in the 4000−400-cm^{-1} frequency range with a resolution of 2 cm^{-1}, using KBr pellets.

Microstructural Characterization. Morphology of the powder samples was observed by means of a field emission scanning electron microscope Hitachi FE S-4100. SEM images were obtained operating at an accelerating voltage of 20 kV.

Elemental Analysis. Si/M (M = Ti, Zr, Hf) ratios in the solids obtained were determined by electron probe microanalysis (EPMA, Philips XL30 ESEM). For it, SiC/MC (M = Ti, Zr, Hf) mixtures with several compositions were prepared from commercial products (Aldrich) and used as standards to quantify the data provided by the instrument. The operating voltage was 10 kV. The free carbon content of the composites was evaluated by standard combustion analysis.

Specific Surface Area. Specific surface areas of solids prepared were determined by the Brunauer−Emmett−Teller (BET) method, using nitrogen adsorption−desorption isotherms recorded on an ASAP 2010 analyzer.

Electron Spin Resonance (ESR). ESR curves were obtained from a Bruker ER 200D spectrometer.

Results and Discussion

TGA curve obtained for a mixture of Cp_2TiCl_2 and PDMS (1:1 weight ratio) (Figure 1a) shows two important weight loss steps, the first one from 120 to about 250 °C (42% weight loss) and the second one between 250 and 450 °C (45.9% weight loss). In addition, very little weight loss is observed between 800 and 1000 °C (1.3% weight loss) and no further weight loss was detected until 1400 °C, resulting in a ceramic yield of 10.8%.

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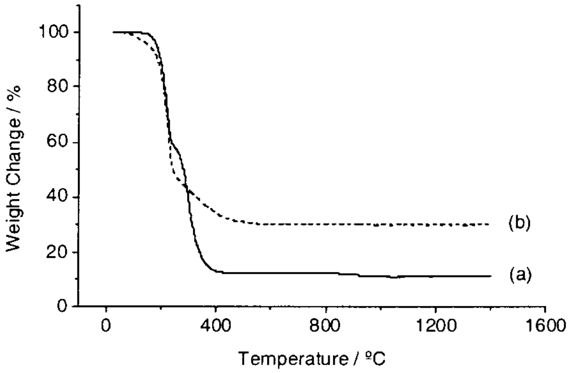

Figure 1. TGA curves for (a) PDMS + Cp_2TiCl_2 and (b) PCS + Cp_2TiCl_2 mixtures (1:1 weight ratio).

The weight loss processes correspond to the partial decomposition of silicon polymer (PDMS) in lower molecular weight components[8] as well as to the partial sublimation and decomposition of bis(cyclopentadienyl) titanium dichloride, which appear overlapped. These two processes are responsible for the low ceramic yield obtained.

That yield is considerably improved when PCS is used instead of PDMS as reveals the TGA recorded for a mixture of Cp_2TiCl_2 and PCS (1:1 weight ratio) (29.9% ceramic yield) (Figure 1b). The existence of reactive Si−H bonds in PCS makes possible the cross-link processes between different chains, thus minimizing the loss of volatile silanes.[8]

For mixtures of Cp_2MCl_2 and PCS it is observed in all cases a first sharp weight loss and a second weight loss smoother than the first one.

We can tentatively propose that the most important processes on which our synthetic method is based are two. On one hand, the cross-linking of PCS chains by means of a dehydrogenation reaction and, on the other hand, the incorporation of the metal by HCl elimination. In addition, partial sublimation of cyclopentadienyl complexes also occurs as well as evaporation of lower molecular weight components.[9b] All these processes, which are responsible for the most important weight losses, occur simultaneously below about 450 °C. At higher temperatures the conversion into the inorganic state goes on and the weight decreases very slowly with temperature until 850−900 °C, depending on the sample.

For all the samples studied the ceramic residues obtained from the mixtures were higher than those resulting from the sum of residues of PCS and Cp_2MCl_2 separately, indicating that the increase in the ceramic residue is due to the reaction of the components of the mixture. A comparison of several compositions for the same metal reveals that as the proportion of metal increases, the ceramic residue obtained decreases, as can be expected taking into account the trend of Cp_2MCl_2 to sublimate. For samples with different metals but with the same weight ratio it is observed that as the atomic weight of metal increases, that is, from titanium to hafnium, the ceramic residue is increased, as can be expected.

The thermal behavior of PDMS and PCS as well as their role as SiC precursors have been extensively treated in the literature.[8,9] On the other hand, the thermal behavior of Cp_2MCl_2 has also been studied, but not to the same extent, although in any case there are some well-known antecedents. Thus, the role of some organometallic precursors of the binary ceramic phases such as TiC, TiN, etc. has been reported.[10] One type of these precursors is the family of bis(cyclopentadienyl)−metal complexes. These molecules show as an advantage versus other inorganic precursors a lower work temperature. Likewise, it has also been indicated that precursors containing cyclopentadienyl groups are interesting because, on one hand, this group confers sufficient stability to the metal complexes, and on the other hand, cyclopentadiene can be eliminated at relatively low temperature and provides a source of carbon when the temperature is increased.

We have also observed in our previous experiences from the thermal analysis of PDMS, PCS, and Cp_2MCl_2 that the ranges of temperatures in which the weight losses of every one of these compounds occur are very close to each other and consequently they must be reactive in a common temperature range. As we mentioned above, both types of materials are suitable as precursors for SiC and MC, respectively. All these facts allowed us to assume that a mixture of them could be used to obtain SiC/MC ceramics. This assumption has been confirmed by the results discussed in this paper.

So we have designed an experimental procedure based on this idea but with some differences with respect to the pyrolysis conditions in which thermal analysis was performed. For the syntheses of M_xCS_y900 ceramic materials we performed a "one pot" route in which PCS is obtained "in situ" from PDMS, previous to the addition of Cp_2MCl_2 and after that the corresponding bis(cyclopentadienyl)−metal complex is added. The mixture is then refluxed, in a quartz tube as is described in the Experimental Section, to minimize the loss of volatile products. According to TG results the conversion of the precursors PCS + Cp_2MCl_2 into the inorganic state is completed at a temperature close to 900 °C, so this temperature was selected for the synthesis of ceramic material. The M_xCS_y900 series of materials are essentially amorphous, as characterized by XRD, SEM, and NMR, although SiC and TiC begin to crystallize, as diffractograms indicate.

We can tentatively propose a possible reactivity model for the first stages of the reaction. Starting from PDMS, it produces PCS as the temperature is increased. PCS, which contains Si−H reactive bonds, produces after H_2 elimination the cross-linking of the chains of the polymer. When we incorporate Cp_2MCl_2 into the reaction, in addition to the above-mentioned reaction, the metal complex can be incorporated into the polymer chains by HCl elimination. So this is probably the way in which metal atoms are incorporated into the network in the first stage. Further steps may be the loss of the organic part of the material to yield finally the inorganic network.

These series of materials were transformed into M_xCS_y1350 series by heating at 1350 °C under an argon atmosphere. From 900 to 1350 °C crystallization of carbide phases progress as is revealed in the powder X-ray diffraction studies.

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Ceramic yields for the syntheses of M_xCS_y900 calculated with respect to the initial amounts of PDMS and Cp_2MCl_2 are presented in Table 1. It must be taken into account that the first step in our procedure implies the conversion of PDMS into PCS and for this process a low yield has been reported.[9a] As we referred those yields to the initial amounts of PDMS, they are logically affected by the yield of the step PDMS to PCS. In addition, during the transformation of PCS into inorganic materials, it has also been reported that in the first stage some lower molecular weight components are removed.[9b]

For all Si/M ratios the thermal treatment produces an enrichment of the ceramics in metal with respect to the precursors. In addition, as the Si/M ratio increases in precursors, the ceramic yield at 900 °C decreases. According to this, we can assume that the loss of volatile silanes is the main cause of the decreasing in yield. There is no significant differences in the Si/M molar ratio between ceramics obtained at 900 and 1350 °C (Tables 1 and 2), this indicating that once the reaction of the precursors is completed, the main components of the ceramics (SiC and MC) do not undergo significant changes. In addition, in M_xCS_y900 some amounts of chlorine were detected by EPMA, whereas M_xCS_y1350 materials are totally chlorine-free. HCl formation was detected during the course of the reaction and probably some amounts of it remained as occluded into the material obtained at 900 °C. The free carbon content (Table 1), as can be expected, increases with the metal proportion because of the higher amount of carbon introduced into the precursor.

X-ray powder diffraction patterns for the M_xCS_y900 series show broad lines due to β-SiC phases. Additionally, broad lines corresponding to the metal carbide (MC, M = Ti, Zr, Hf) phases were also detected in the diffractogram. This broadening must be associated with a partially amorphous state, according to that observed by SEM. The X-ray powder diffraction spectra for M_xCS_y1350 materials indicate a more crystalline state, confirmed by SEM, also showing only lines due to β-SiC and MC (M = Ti, Zr, Hf) and provide no evidence of any oxide phase, according to a totally non-oxidic material. This was confirmed by the infrared spectra, which exhibit for all the ceramics a strong band at about 800 cm^{-1}, characteristic of the Si–C stretch,[2] no Si–O bands being observed. Figure 2 shows diagrams for the M_xCS_y1350 series. For the three metals it is observed, as can be expected, that as the M proportion increases, the intensity of the peaks corresponding to MC increases whereas that of peaks of SiC decreases, as shown in Figure 3 for samples with zirconium.

From the XRD patterns obtained for M_xCS_y1350 materials SiC/MC ratios were determined as described in the Experimental Section. The obtained values match very well the Si/M ratios determined by EPMA.

Because of the partial amorphous nature of the products, they can be more appropriately characterized by means of solid-state NMR spectroscopy which has been revealed as a powerful tool for the characterization of crystalline and amorphous ceramic materials.[11]

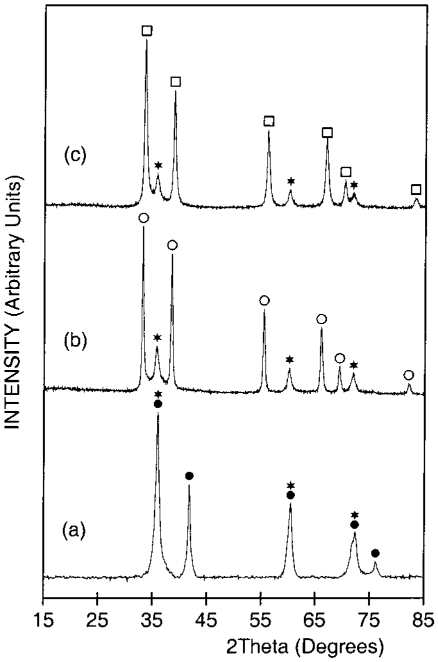

Figure 2. X-ray powder diffraction diagrams of: (a) TCS1350, (b) ZCS1350, and (c) HCS1350. β-SiC, ★; TiC, ●; ZrC, ○; HfC, □.

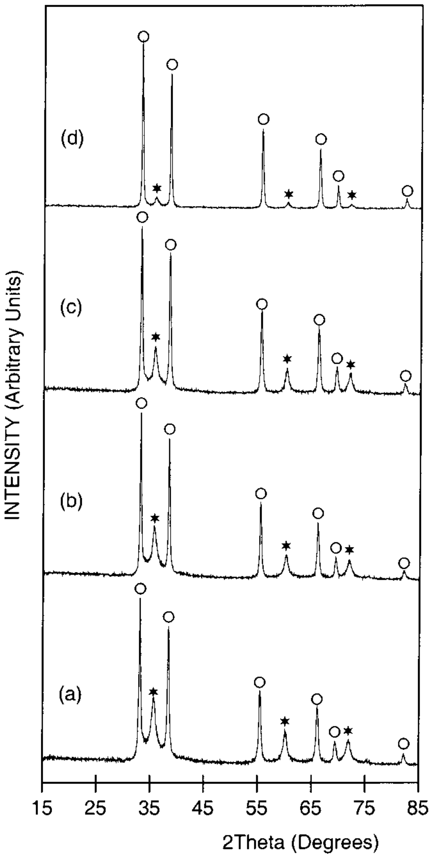

Figure 3. X-ray powder diffraction diagrams of (a) ZCS_21350, (b) $ZCS_{1.5}1350$, (c) ZCS1350, and (d) $Z_2CS1350$. β-SiC, ★; ZrC, ○.

The solid state ^{29}Si MAS NMR spectra for M_xCS_y900 materials show a broad signal (centered between −5.1 and −9.8 ppm) (Figure 4). These chemical shift values are in accordance with a SiC_4 environment for silicon. The broadening of the signal observed can be associated

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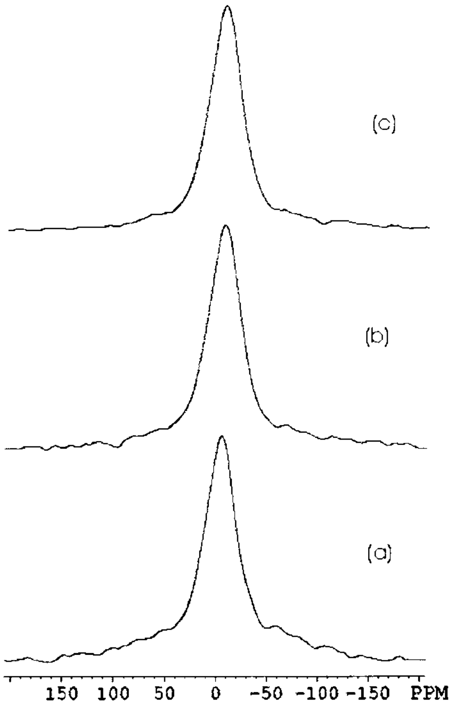

Figure 4. ^{29}Si MAS NMR spectrum of (a) TCS900, (b) ZCS900, and (c) HCS900.

with a low crystallization grade, as indicated by XRD and SEM. These data suggest that M_xCS_y900 materials have an amorphous silicon carbide based structure. The composition or the nature of the metal hardly have any influence on the chemical shift.

For M_xCS_y1350 materials the ^{29}Si MAS NMR spectra consist of a set of three signals (a first intense peak from −14.9 to −15.7, a second from −18.9 to −19.5, and a third from −23.7 to −24.7, both of them less intense than the first one) as Figure 5 shows. For these materials no dependence of chemical shift on composition and metal atom was found. The presence of various peaks in the ^{29}Si NMR spectrum for silicon carbide has been related to the existence of different polytypes which have been characterized by NMR spectroscopy.[12] Effectively, the presence of an only peak between −14 and −18 ppm is assigned in the literature to β-SiC, the cubic form of SiC, and the existence of three peaks with similar intensities between −14 and −30 ppm is assigned to α-SiC polytypes. Thus, it has been reported in the literature[12a] that signals between −18 and −30 ppm are assigned to a mixture of α-SiC polytypes, whereas a signal at −16 ppm is assigned to β-SiC. On the other hand, it has been reported that the SiC obtained by pyrolysis of poly(methylsilane) (PMS)[13] shows in the ^{29}Si MAS NMR spectrum a set of signals at −15.7, −20.5, and −24.9 which has been assigned to a mixture of β-SiC and small amounts of α-SiC. This spectrum is very similar in chemical shift and relative intensities of the different peaks to those obtained by us. It has also been reported that, for SiC/TaC ceramics obtained by carbothermal reduction up to 1600 °C of a tantalum ethoxide modified PCS,[14] the ^{29}Si MAS NMR spectrum consists of a single signal which has been assigned to β-SiC.

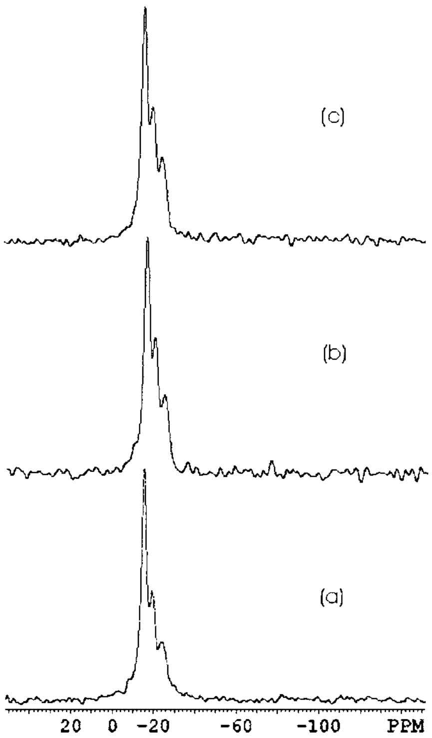

Figure 5. ^{29}Si MAS NMR spectrum of (a) TCS1350, (b) ZCS1350, and (c) HCS1350.

According to this, in our case, the most intense peak at about −15 ppm corresponds to β-SiC and small amounts of α-SiC, and the other two peaks at −19 and −24 ppm, much less intense than the first, correspond to α-SiC.

According to those above-mentioned NMR results and taking into account that peaks which could correspond to SiO_x are not detected, we can assume that in our material silicon is forming part of the C_4Si units in a silicon carbide based structure. In M_xCS_y1350 materials silicon is mainly present as β-SiC, accompanied by small amounts of α-SiC.

We also studied the M_xCS_y900 and M_xCS_y1350 materials by ^{13}C MAS NMR spectroscopy. All the materials show a signal in the range of 15−20 ppm which can be attributed to a CSi_4 structure. In addition, a very broad signal at about 130 ppm corresponding to graphitic carbons is also observed.

ESR experiments show a signal at $g = 2.0024$ for all the pyrolyzed products. This signal has been reported for oxycarbide glasses,[15] silicon carbide,[16] silicon ni-

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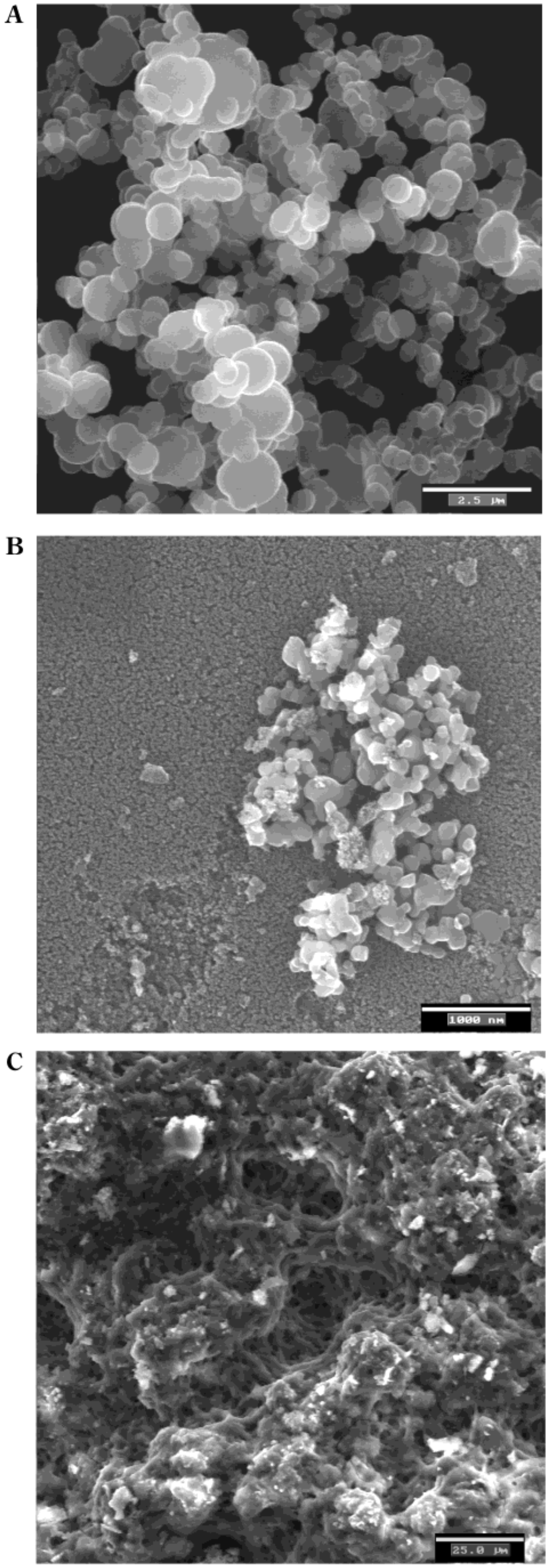

Figure 6. Scanning electron micrographs of (A) TCS900, (B) TCS1350, and (C) TCS1350, prepared directly by pyrolysis at 1350 °C of a 1PDMS:$1Cp_2TiCl_2$ mixture.

tride,[17] and silicon carbonitride[18] obtained from different precursor systems. It has been suggested[15] that, during the decomposition of the organic groups, radicals such as C· are formed. These radicals are responsible for the ESR signal.

Morphology of the final ceramic materials, observed by scanning electron microscopy, confirms the above-discussed results on XRD and NMR. The low-temperature materials M_xCS_y900 are essentially amorphous (Figure 6A). For materials obtained at 1350 °C crystallization becomes evident (Figure 6B), although a part of the material remains in the amorphous state.

On the other hand, recently, there has been an increasing interest in SiC and related materials as catalytic supports.[19,20] This interest is based on several advantages which these solids show when they are compared to conventional oxidic supports: high thermal stability, chemical inertness, and low thermal expansion. For these reasons, it is of interest to prepare SiC-based materials with high surface areas and with resistance to the sintering phenomenon. In this sense, we have obtained some preliminary data about the BET surface area of M_xCS_y900 and M_xCS_y1350. These materials show very little surface areas. However, if TCS1350 is prepared directly by pyrolysis at 1350 °C of a 1PDMS:$1Cp_2TiCl_2$ mixture a product with a relatively high BET surface area of 134 ± 2 m^2/g is obtained. Scanning electron microscopy for this material (Figure 6C) shows a porous appearance in good agreement with the value of surface area measured. The remarkable fact is that, in contrast to the previously described SiC-based solids[20] for which the reported surface area is near 50 m^2/g after calcination at about 550 °C, our carbide material shows its high surface area after calcination at 1350 °C. Unfortunately, materials prepared by this method are obtained in very low yield. Studies directed at preparing high surface area materials with better yields are now in progress.

The results obtained allow us to conclude that the combination of a silicon polymer, PDMS or PCS, and bis(cyclopentadienyl)−metal complex can be considered as a suitable new precursor for SiC/MC-based ceramics with M = Ti, Zr, and Hf. The absence of oxygen in the composition of the precursor mixture is an advantage since a carboreduction process, which usually requires higher temperatures, is not necessary, thus allowing the conversion of precursors into ceramics to occur at a relatively low temperature, such as 900 °C.

Finally, we conclude that this work opens a new synthetic route toward the preparation of new SiC/MC ceramics based on the use of different members of the family of the bis(cyclopentadienyl) complexes as the metal source.

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