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Plasma polymerization of ferrocene with silane and silazane monomers for design of nanostructured magnetic ceramics

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The synthesis and characterization of nano-metallopolycarbosilanes (nMPCS) and their transformation into ceramic materials was reported. Plasma polymerization proved to be a useful tool in the synthesis of inorganic polymer precursors for design of ceramics with induced multiscale organization and shaped ceramics with tunable magnetic properties. The genesis of nanostructured, magnetically tunable ceramics using low-molecular-weight inorganic plasma polymers is a simple alternative to the chemical route. The present is concerned with advantages offered by plasma assisted chemical vapor deposition systems (PACVD) coupled with chemical transport reaction (CTR) for synthesis of copolymers based on ferrocene with hexamethyldisilane (HMDS) and hexamethyldisilazane (HMDSz) monomers and their transformation into ceramic materials. Pyrolysis with subsequent moderate temperature sintering under argon/nitrogen atmospheres at 1200 °C leads to nanostructured magnetic ceramics. The pre-ceramic polymers and resulted ceramic characterized with SEM, XRD and Raman spectroscopy to gain information of their morphology, crystallinity and composition with regard to the deposition parameters. In addition, magnetic properties are taken in account to evaluate the performances of these materials.

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1. Introduction

Recently, the inorganic polymers have become an exciting topic due to the potential applications either theirs the intrinsic properties (magnetic, electrical, optical, and catalytic) or precursors in advanced nanostructured ceramics. The properties that make them different are associated with metal containing in the backbone or in side-parts.

Pyrolysis of polymer precursors allows to designing ceramics with an induced composition, structuring at nanometric scale and advanced properties [1-3]. This is imited by classical methods based on micro and nanopowder sintering. The pyrolysis of the inorganic polymer precursors combined with sintering could be an alternative method to obtain nanostructured ceramics exhibiting high temperature stability, high creep resistance, retarded crystallization behavior and low oxidation rates [4-6].

The most important issue in nanostructured ceramics is that the properties are tunable function of polymers and nanophase precursors in agreement with the final phase diagram using a suitable pyrolysis-sintering process. In particular for this contribution when are used polymer precursors in presintering process are released compounds at molecular and nanometric scale ready to sintering. The by products in different stages can play also a local inert or reactive atmosphere which is sometimes beneficial for final ceramics induced properties.

Besides these incontestable advantages in ceramics field where the properties are accordable function of the initial polymer precursors the chemical route to get inorganic polymers with a predefined architecture is not an easy and productive one, for this reason plasma polymerization could be an appropriate alternative to chemical route.

Plasma polymerization proved to be a useful tool in the synthesis of inorganic polymer precursors for design of ceramics with induced multiscale organization and shaped ceramics with tunable magnetic properties. The genesis of nanostructured, magnetically tunable ceramics using low-molecular-weight inorganic plasma polymers is a simple alternative to the chemical route [7-9].

The contribution concerns with advantages offered by an improved configuration plasma assisted chemical vapor deposition (CVD) coupled with chemical transport reaction (CTR) for synthesis of copolymers based on ferrocene with hexamethyldisilane (HMDS) and hexamethyldisilazane (HMDSz) monomers and their transformation into ceramic materials. Pyrolysis under argon/nitrogen atmospheres at 1200 °C leads to nanostructured magnetic ceramics.

SEM, TEM, SAED and XRD methods were used to gain information of morphology, crystallinity and composition of pre-ceramic polymers and corresponding resulted ceramics with regard to the deposition parameters.

2. Experimental

Pre-ceramic polymers were obtained by plasma assisted chemical vapor deposition of hexamethyldisilane (HMDS) with ferrocene and hexamethyldisilazane (HMDSz) with ferrocene monomers.

A proprietary method was used for plasma polymerization consisting of a RF-glow discharge reactor (quartz tube 1 m length, 60 mm diameter) coupled with a heater to accommodate a specific backbone structure in the polymer precursor. The experimental technique was described elsewhere [7]. This experimental arrangement gives the possibility to build polymers with different type of precursors in mixture or separate with a precise control of the dosage.

In our specific case to produce polycarbosilanes-ferrocene copolymers with a defined composition, we select the next configuration: HMDS was atomized in argon plasma stream and a small pellet ferrocene (4 grams) was positioned into the quartz tube in front of the heater where temperature was 250 ^oC. For 2 h, ferrocene was consumed by plasma etching and very slow evaporation. In this time, HMDS (5ml) was sequential atomized in quantity of 4-4.5 μl/min. The argon flow was established at 1300 sccm/min, plasma power to 240 W (frequency 2.5 MHz), pressure p= 1.3-2 KPa. A grayish copolymers powder was collected and indexed as PCSFc. In the same experimental configuration, polycarbosilazanes-ferrocene copolymers are achieved by replacing the HMDS with HMDSz monomers and following deposition parameters: argon flow 1300 sccm/min, plasma power to 360 W (frequency 2.5 MHz), pressure p= 6.7-7.9 kPa. A grayish colour powder was collected and noted PCSzFc.

PCSFc powder, placed in an alumina crucible, was thermal treated at 1200 ^oC with 5 ^oC/min under argon atmosphere. The soaking time, was 1h. Finally, the sample was cooled in air to room temperature. The resulted ceramics called Fe -Si-C shift color to grayish-brown.

PCSzFc powder, placed in an alumina crucible, was thermal treated at 1200 ^oC with 5 ^oC/min under nitrogen atmosphere. The temperature was raised for 3h at 1200 ^oC, 4h- soaking time, free cooling to RT. The resulted ceramics change color to brown and was called Fe-Si-C-N.

The pre-ceramic and ceramic materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and (SAED). XRD pattern of the samples was collected using Bruker D8-Advance powder diffractometer, CuKα radiation (λ=1.548 Å) and equipped with a copper target X-ray tube and a diffracted-beam monochromator. Philips CM120ST (Customized Microscope 120 Super Twin) was used for collecting the transmission electron microscopy and selected area electron diffraction images. SEM investigations have been performed with a FEI-Quanta 400 scanning electron microscope. In addition, magnetic properties are taken in account to evaluate the qualities of these materials.

3. Results and discussion

The atypical diffraction pattern of pre-ceramic materials PCSFe obtained form HMDS and ferrocene precursors (Fig. 1a) is due to the experimental set-up used for synthesis, a RF-glow discharge reactor coupled with a heater. Taking into account the working temperature of the heater (500 ^oC-in the middle point and 250 ^oC in the deposition region) and the deposition time, the pre-ceramic materials are different from the classical polymers because structural modifications took place. In the agreement with these expectations, small clusters with predefined Fe-Si-C in a matrix of carbosilanes were obtained. In consequence, XRD pattern of PCSFc reveals a predominant phase close to the iron silicon carbide (Fe-Si-C), Fe_3Si and Fe_3C, which are confirmed by SAED images (Fig. 2e), identified from ICDD 1999- International Center for Diffraction Data.

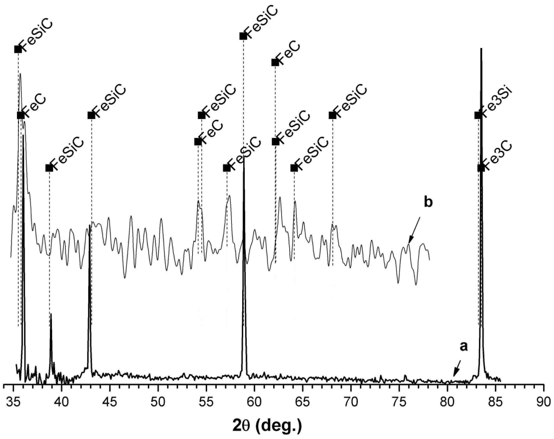

Fig. 1. XRD patterns of: a) preceramic material, PCSFc and b) ceramic material, Fe-Si-C.

The multiscale organization of preceramic material PCSFc (Fig. 2) give morphological information in the 20 μm-50 nm range. The surface of PCSFc show a granular texture, which corresponds to the transition towards micrometric aggregates, made of nanometric round-shape particles (Fig. 2).

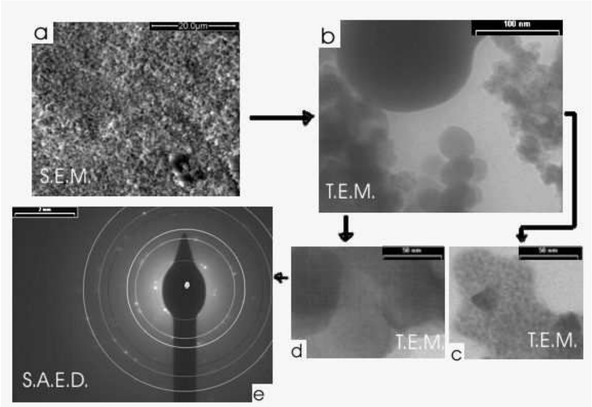

Fig. 2. Multiscale organization for pre-ceramic material, PCSFc: (a) scanning electron microscopy image; (b, c, d) transmission electron microscopy image; (e) selected area electron diffraction pattern.

The preceramic obtained by using these precursors loses the rest of organic material being easily converted into nanostructured ceramic materials (Fe-Si-C). Fig. 1(b) shows a predominant phase close to iron silicon carbide (FeSiC) and other phases, which may be present in the material Fe-C (the pattern presenting high fluorescence due to iron content was difficult to reproduce at phase analysis). This is in agreement with the corresponding

SEM, TEM and SAED analysis (Fig. 3), which prove the presence of two different phases in the resulted ceramic materials. SEM images show the tapped powder of PCSFc (Fig. 3a) is converted to well-shaped spherical structure.

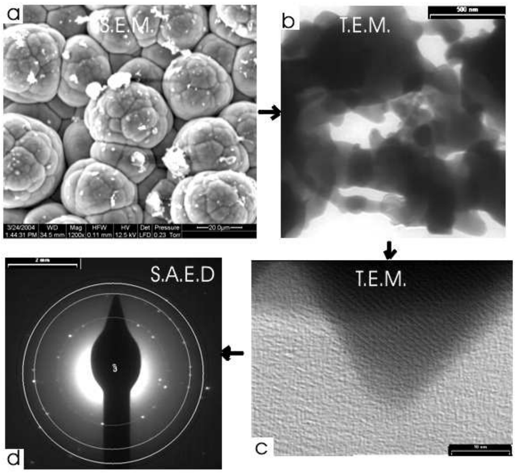

Fig. 3. Multiscale organization for ceramic material, Fe-Si-C: (a) scanning electron microscopy image; (b, c, d) transmission electron microscopy image; (e) selected area electron diffraction pattern.

In the case of pre-ceramic materials PCSzFc obtained from HMDSz and ferrocene precursors and based on above mentioned considerations about experimental set-up, the XRD patterns reveals two phases being close to Fe_2N and SiC (Fig. 4a). The multiscale organization, characteristic of pre-ceramic polymers and resulted ceramic, is studied over more than three orders of magnitude by using scanning electron microscopy (SEM) which give morphological information in the 20 μm -5 μm range and TEM (resolution in the lattice fringe mode: 0.2 nm) (Fig. 5). The surface of PCSzFc exhibits a granular texture, which corresponds to transition towards micrometric aggregates made of di-phasic nanometric round-shape particles (Fig. 5b and Fig. 5c). The texture at nanometric scale evidences that there are two types of compounds with a specific organization.

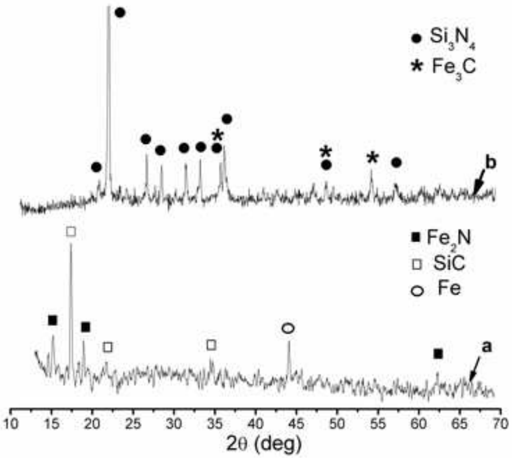

Fig. 4. XRD patterns for: a) preceramic material, PCSzFc and b) ceramic material, Fe-Si-C-N.

The ceramics Fe-Si-C-N resulted from PCSzFc, by pyrolysis raises to more compact materials containing well-developed phases as shown in Fig. 5g and Fig. 5h close to Si_3N_4 and Fe_3C compounds. That is in concordance with X-ray diffraction and SAED observations (Fig. 4b and Fig. 5j). SAED and XRD pattern reveals a series of diffractions lines coincident with Si_3N_4 and Fe_3C structures (identified from ICDD 1999-International Center for Diffraction Data).

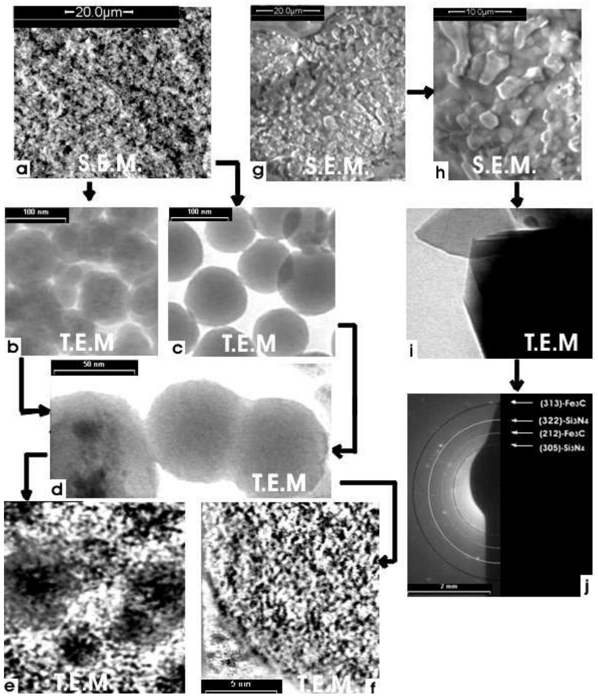

Fig. 5. Multiscale organisation in PCSzFc: (a) scanning electron microscopy image; (b, c) low magnification transmission electron microscopy image; (d) high resolution transmission electron microscopy image; (e, f) high resolution transmission electron microscopy image represented in bright field and for ceramic material, Fe-Si-C-N: (g,h) scanning electron microscopy image; (i) low magnification transmission electron microscopy image; (j) selected area electron diffraction pattern.

Magnetic behavior of preceramic and ceramic materials. Magnetic measurements of pre-ceramic and ceramic materials obtained from HMDs and ferrocene precursors were carried out using a KLY-3Kappa Bridge AGICO (sensibility 10^{-8} SI) and micro-MAG Alternating Gradient Magnetometer M 2900 and show ferromagnetic behaviors in the both cases. Field-dependent magnetization curves show a hysteresis loop and a saturation maximum at 0.2 mT (Fig. 6a). The hysteresis loop of pre-ceramic materials-PCSFc is narrowed than in ceramic materials. In addition, the susceptibility function of temperature showed for PCSFc a ferromagnetic component, with the Curie temperature around of 140 K, and a paramagnetic component (Fig. 6b), which was not observed in Fe-Si-C ceramic materials.

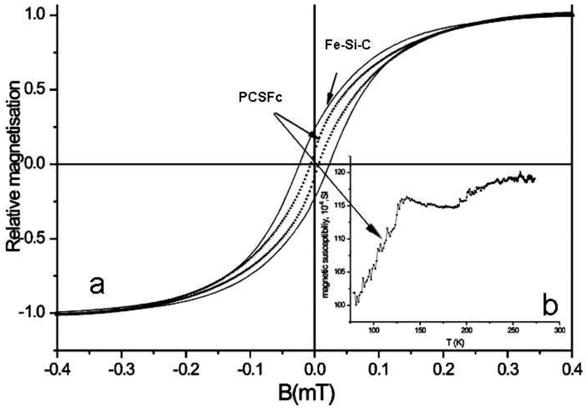

Fig. 6. Magnetic behavior for PCSFc and Fe-Si-C samples: (a) hysteresis loop given in relative magnetization, (b) susceptibility.

For PCSzFc and Fe-Si-C-N the isothermal remanent magnetization (IRM) acquisition and demagnetization was performed using a Magnon International pulse magnetizer up to a maximum field of 2 T. Bcr, coercivity of remanence, was determined from demagnetization curve. Thermomagnetic measurement were performed in air up to 800 °C on a modified horizontal translation type Curie balance with a noise level of 5 × 10^{-9} Am^2 [10]. The measurement method allows for the separation of ferromagnetic and paramagnetic contributions.

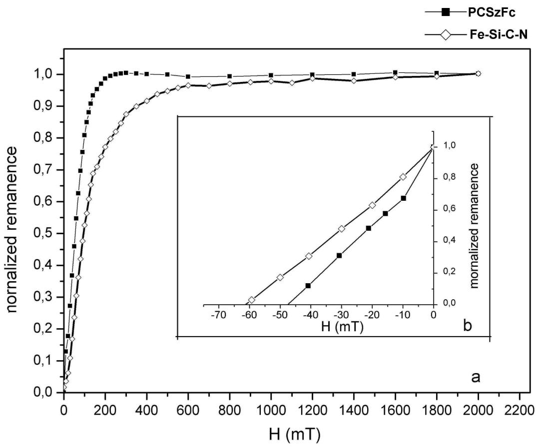

Fig. 7. a) IRM acquisition and b) demagnetization curves for PCSzFc and ceramic Fe-Si-C-N.

Magnetic measurements performed on PCSzFc and Fe-Si-C-N reflects the two different Fe compounds: Fe_2N and Fe_3C. Fe_2N has a significant acquisition of IRM in low fields (Fig. 7). It was fully saturated in a magnetic field of 275 mT and has a Bcr of 48 mT. These values are similar with those reported for Fe_2N by Choi et al. [11]. Thermomagnetic curve show a significant decrease until around 300 °C and any ferromagnetic contribution disappear after 400 °C (Fig. 8A). We estimate that the Curie temperature of Fe_2N is probably is in this temperature interval. Further heating up to 800 °C produce important chemical changes and the cooling curve is dominated only by the paramagnetic component. The absence of a clear Curie temperature around 770 °C, characteristic for iron, suggests that this component present in XRD pattern is not important for the bulk magnetic properties of PCSzFc.

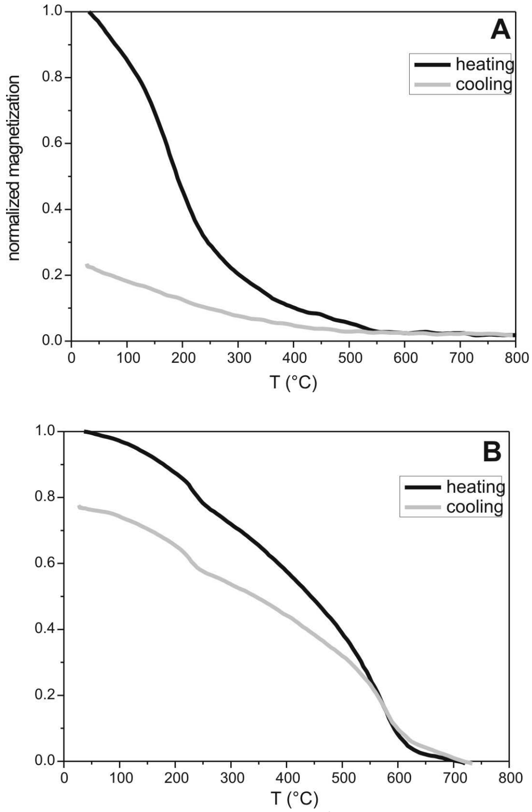

Fig. 8. Total thermomagnetic curves for: (A) PCSz-Fc and (B) Fe-Si-C-N.

The formation of Fe_3C structures by pyrolysis is reflected in a different coercivity spectrum than Fe_2N during the acquisition of IRM and by an increase of Bcr at 60 mT (Fig. 7). The sample was 96% saturated in a field of 0.7 T, but it displayed continued acquisition of IRM up to 2T. This can be an indication about the presence in the ceramics of two magnetic phases with different coercivities. Thermomagnetic curve show also the presence of two components (Fig. 8B). The first one is reflected by the change in slope between 200 °C and 250 °C, which suggest a Curie temperature in this interval. The second has significant higher Curie temperature around 600 °C. The cooling curve shows that the ferromagnetic components are not significantly affected by the heating at 800 °C. The interval for the first Curie temperature includes the usually reported Curie temperature for Fe_3C of 210 °C [12]. The second Curie temperature, around 600 °C, is closed to Curie temperature reported for passivated Fe_3C nanoparticles made by laser pyrolysis by Grimes et al. [13]. They suggest that this enhanced Curie temperature is associated with an outer coating of carbon surrounding the nanoparticle. According to the data presented by Grimes et al. [13] the coercivity found in our experiment is compatible also with a mixture of these two ‘phase’ of Fe_3C. In the acquisition curve of IRM we associate the soft component with the Fe3C having the normal Curie temperature (210 °C) and the hard component with the Fe_3C characterized by enhanced Curie temperature.

4. Conclusions

The specific experimental set-up proved to be a useful tool in the synthesis of preceramic materials for design of ceramics with induced multiscale organization and shaped ceramics with tunable magnetic properties.

In both cases either PCSFc or PCSzFc preceramic materials, pyrolysed under argon/nitrogen atmosphere, they are converting in multiphase ceramics. Both polymers have a nanometric round-shaped particles, large governed by hydrogen bonds which rise to a low-density spherules. Depending of initial composition the resulted ceramics can be accommodated in a large area of composition and structures.

In addition, the magnetic investigations give interesting potential applications either for preceramics materials or ceramics materials obtained from ferrocene with hexamethyldisilane (HMDS) and hexamethyldisilazane (HMDSz) precursors using an improved configuration for experimental set-up.

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